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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -- Publisher.

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CONJUNCT PHENYLATION OF TRICHLOROSILANE AND SILICON TETRACHLORIDE

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The synthesis of phenyltrichlorosilane can be varied out by the interaction of silicon tetrachloride and organic compounds of mercury, sodium, and magnesium [1], and also by the interaction of trichlorosilane and benzene under pressure according to the scheme:

$$HSiCl_3 + C_6H_6 \rightarrow C_6H_5SiCl_3 + H_2. \quad (1)$$

The latter reaction has been carried out in the presence of aluminum chloride and boron trifluoride [2, 3] and also in the absence of catalysts [4]. However, the maximum yield attainable in this reaction does not exceed 40% of theoretical, calculated on the reacted trichlorosilane [5]. This is due to the necessity of using elevated temperatures and pressures (300-460° and 150-200 atm, gauge) at which, along with reaction (1), disproportionation takes place leading to the formation of silicon tetrachloride (up to 40 mole % of the reacted trichlorosilane) and other byproducts.

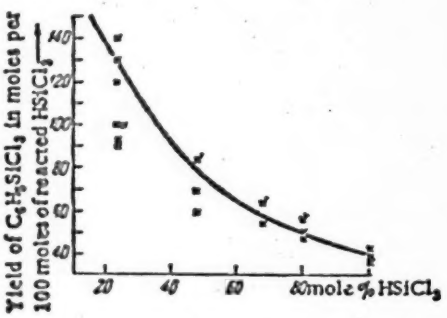

Fig. 1.

The study of methods of supressing these side reactions and also the study of the possible phenylation of the carbon tetrachloride formed are of great interest. In searching for a solution to the problems, we carried out experiments on the hydrogenation of silicon tetrachloride, and we found that the reaction proceeds rather vigorously according to the scheme:

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl \quad (2)$$

when the reactants are heated under conditions under which phenylation of trichlorosilane is carried out (440-460° and 180 atm, gauge). The results showed that it is basically possible to phenylate silicon tetrachloride if conditions are provided such that it is first converted to trichlorosilane and then reacts with the benzene. In carrying out the first stage of the process, we made use of the hydrogen formed by reaction (1) and present as unconsumed byproduct of the phenylation of trichlorosilane. The reaction was carried out by heating a mixture of silicon tetrachloride, benzene, and trichlorosilane [6] at 440°, a pressure of 180 atm, gauge, and a mole ratio of trichlorisilane to silicon tetrachloride of 0.25 : 0.75 to 0.85 : 0.15.

Figure 1 presents the results of a series of experiments showing that the yield of phenyltrichlorosilane (in moles per 100 moles of reacted trichlorosilane) sharply increases with an increase in the silicon tetrachloride content of the mixture. Such an increase cannot be explained solely by supression of the disporportionation of

trichlorosilane and the resultant formation of silicon tetrachloride, since in some of the experiments the yield of phenyltrichlorosilane significantly exceeded 100 moles per 100 moles of trichlorosilane. This indicates that silicon tetrachloride enters into the phenylation reaction according to the scheme:

$$\begin{array}{l} SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl \\ HSiCl_3 + C_6H_6 \rightarrow C_6H_5SiCl_3 + H_2 \\ \hline C_6H_6 + SiCl_4 \rightarrow C_6H_5SiCl_3 + HCl \end{array}$$

The use of increased hydrogen pressure facilitates the occurrence of the first stage of the phenylation of silicon tetrachloride – the hydrogenation stage. In this connection, the yield of the final product, phenyltrichlorosilane, calculated on the silicon tetrachloride proved to be significantly higher than when a mixture of benzene and silicon tetrachloride was passed through a heated tube at atmospheric pressure.

Thus, it has been shown experimentally that the phenylation of silicon tetrachloride with benzene can take place in the absence of organometal compounds, with ample yields, if conditions are provided such that the silicon tetrachloride is hydrogenated and thereby converted to an intermediate reaction product, trichlorosilane, in accordance with Eq. (2). The latter compound reacts with the benzene with the formation of phenyltrichlorosilane, and the hydrogen is regenerated.

EXPERIMENTAL

Hydrogenation of Silicon Tetrachloride. A 20-liter autoclave was charged with 4.00 kg of silicon tetrachloride, and hydrogen was admitted to a pressure of 52 atm. The autoclave was heated to a temperature of 440° over a period of 6 hours, and was held at this temperature for 4 hours, during which there was a gradual increase in the pressure to 180 atm. After the autoclave had cooled to room temperature, the residual hydrogen (47 atm, gauge) was vented, and 3.36 kg of reaction products was discharged from the autoclave. Distillation of the mixture from a flask fitted with a dephlegmator yielded 697 g of a fraction boiling at 30-55°. A second distillation of this fraction in a fractionating column with an efficiency of 45 theoretical plates yielded 266 g of fraction boiling at 31-32°.

Found % H 0.74; 0.73; Cl 79.0; 78.9. $HSiCl_3$. Calculated % H 0.74; Cl 78.8

Phenylation of Trichlorosilane and Silicon Tetrachloride. A 0.6 liter autoclave was charged with a mixture of 90 g of benzene, 17 g of trichlorosilane, and 68 g of silicon tetrachloride. The mixture was heated for 4 hours at 460° (the pressure increased to 170 atm, gauge); the reactor was then cooled to room temperature, the residual hydrogen (10 atm at room temperature) was vented, and 168 g of reaction products was discharged from the autoclave. Fractionation of the mixture in a column with an efficiency of 45 theoretical plates yielded the following fractions:

Fraction	B.p., °C	Yield, %	Cl content, %
1	34 — 55	2,7	83,0
2	55 — 57	28,6	83,3
3	57 — 79	1,8	56,1
4	79 — 80	39,2	1,5
5	185 — 190	7,6	49,9
6	190 — 200	11,5	50,2
Residue		1,9	40,2

Fractions 1 and 2 were silicon tetrachloride (traces of trichlorosilane were present in fraction 1); fraction 3 was intermediate cut; fraction 4 was benzene with traces of silicon tetrachloride; and fractions 5 and 6 were phenyltrichlorosilane (benzene was present as an impurity in fraction 5). The yield of phenyltrichlorosilane was 139 moles per 100 moles of trichlorosilane charged.

Figure 1 presents data from a series of experiments carried out by a similar method but with the use of different ratios of trichlorosilane to silicon tetrachloride.

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* Original Russian pagination. See C. B. translation.

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REACTION OF PYRIDINE-3,4-DICARBOXYLIC ACIDS WITH HYDRAZINE AND ANILINE

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(Presented by Academician B. A. Kazanskii, November 10, 1959)

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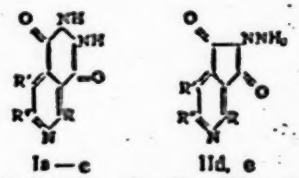
During an investigation of the reaction of derivatives of oxazole with maleic anhydride [1], we prepared some new pyridine-3,4-dicarboxylic acids. The present paper describes the condensation of these acids with hydrazine and aniline.

The presence of two neighboring carboxyl groups in the molecule of these acids suggests that certain types of derivatives would be obtained; in similar cases, the chief direction of the process is determined by the individual peculiarities of the original compounds. Thus, esters of the simplest o-dicarboxylic acids of the benzene series and of five-membered heterocycles (with the exception of thiophene) react with hydrazine to form dihydrazides; esters of thiophenedicarboxylic acids yield cyclic hydrazides [2]; and the anhydride of 3,6-diphenylphthalic acid yields only the N-aminoimide [3]. Cyclic hydrazides were obtained from esters of the previously known pyridine-3,4-dicarboxylic acids (the unsubstituted [4] and the 2,6-dimethyl-substituted [2] acids) and also from the anhydride of quinolinic acid [5] when these compounds were reacted with hydrazine, although it was noted that the free quinolinic acid does not form a cyclic compound. Our investigation showed that when 5,6-dimethyl-, 2,6-dimethyl-, and 5-hydroxy-2-methylpyridine-3,4-dicarboxylic acids are heated, even briefly, with hydrazine, they are converted to the cyclic hydrazides (pyrido-3,4-pyridazinediones) I in yields of 60-80%, but in the case of 2,5,6-trimethylpyridine-3,4-dicarboxylic acid, this same reaction leads to the formation of the N-aminoamide of the acid II.



Ia—e IId, e

a) R = H, R′ = R″ = CH_3; b) R′ = H, R = R″ = CH_3; c) R′ = OH, R = CH_3, R″ = H;
d) R″ = H, R = R′ = CH_3; e) R = R′ = R″ = CH_3.

Treatment with hydrazine of 2,5-dimethylpyridine-3,4-dicarboxylic acid, in which the COOH groups are just as blocked as in the 2,5,6-trimethyl analog, yields the N-aminoimide II d with a small amount of hydrazide I d. Prolonged heating of the reaction mixture leads to a change in its composition, the content of the aminoimide gradually decreasing and the yield of the hydrazide increasing to 60%. Isomerization of the aminoimide is accelerated by the presence of unreacted hydrazine, since pure II d in an inert medium is isomerized only to the extent of 10% under the same conditions.

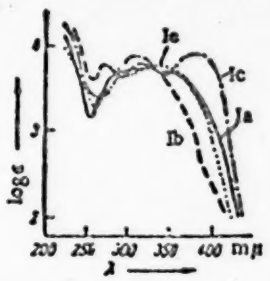


Fig. 1

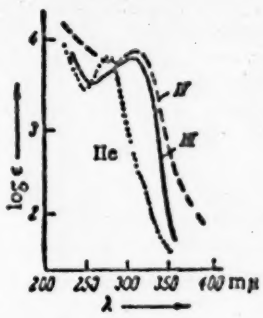


Fig. 2

Fig. 3

In contrast to the 2,5-dialkyl-substituted acids, 5-hydroxy-2-methylpyridine-3,4-dicarboxylic acid reacts with hydrazine to yield exclusively hydrazide II c. The formation of a new six-membered ring in this case is apparently explainable on the basis that the position of the OH group is such that it is oriented oppositely to the carboxyl, while such a configuration cannot exist in the 5-methyl derivatives.

The most stable derivatives of pyridine-3,4-dicarboxylic acids are the cyclic hydrazides I. For example, hydrazide I e is formed as the end reaction product during the action of hydrazine on the acid (after rearrangement to the aminoimide), its amide, and its N-phenylimide. Hydrazide I a was obtained in high yields by the treatment of the free acid, its diamide, and its dimethyl and also monomethyl esters with hydrazine. An attempt to use the monoester for the preparation of the acyclic monohydrazide resulted only in the formation of I a. The cyclic hydrazides of pyridine-3,4-dicarboxylic acids are light-colored, high-melting compounds which are very stable and are insoluble in organic solvents; they are soluble in aqueous ammonia, mineral acids, and hot acetic acid, and they are titrated by aqueous solutions of bases rather like monohydric phenols (the hydrazide of 5-hydroxy-2-methylpyridine-3,4-dicarboxylic acid titrates like a dihydric phenol).

A weak luminescence was observed when alkaline solutions of the hydrazides of alkylpyridinedicarboxylic acids were oxidized with hydrogen peroxide, but the solution of I c luminesced strongly. Like the analogous compounds of the phthalazine series, the pyridopyridazinediones yield monochlorides upon treatment with $POCl_3$, and they are alkylated by esters of toluenesulfonic acid.

Figure 1 presents the absorption spectra of hydrazides I a (λ_{max} 312 mμ, log ϵ_{max} 3.72) I b (λ_{max} 270 and 310 mμ, log ϵ_{max} 3.78; 3.79), I c (λ_{max} 306 and 375 mμ, log ϵ_{max} 3.79, 3.93; and I e (λ_{max} 288 and 328 mμ, log ϵ_{max} 3.73; 3.79).

The substituted N-aminoimides are insoluble in aqueous bases, but dissolve in alcohols. When heated in the presence of basic catalysts they are converted to the isomeric hydrazides, while they yield condensation products with aldehydes. The ultraviolet absorption spectra of the N-aminoimides differ from the spectra of the hydrazides and are similar to the spectra of the corresponding imides which are unsubstituted at the nitrogen, and also to the spectra of N-phenylimides. The absorption curves of 2,5,6-trimethylpyridine-3,4-dicarboximide (III) and the N-phenylimide (IV) (Fig. 2) have practically coincident maximums (308 and 310 mμ) and only slightly differing values of the absorption coefficient (log ϵ_{max} 3.83 and 3.88); they are very similar to the curve for the N-aminoimide of this acid. A change in the degree of substitution in the pyridine part of the molecule (Fig. 3, spectra of aminoimide II d (λ_{max} 272 mμ; log ϵ_{max} 3.69) and 2,5-dimethylpyridine-3,4-dicarboxylic acid N-phenylimide (V) (λ_{max} 300 mμ, log ϵ_{max} 3.78) likewise causes only a small shift in the maximum and does not alter its character.

The authors express their deep appreciation to Academician B. A. Kazanskii for his attention and aid during completion of the present work and to L. A. Kazitsyna for carrying out the spectroscopic investigation.

EXPERIMENTAL

2,5,6-Trimethylpyridine-3,4-dicarboxylic acid N-aminoimide (IIe). A mixture of 6 g of 2,5,6-pyridine-3,4-dicarboxylic acid and 1.5 g of hydrazine hydrate was heated in 10 ml of ethylene glycol for 15 minutes. The yield of IIe was 60% m.p. 211-212° (from methanol).

Found %: C 58.74; 58.88; H 5.48; 5.51; N 20.70; 20.20 $C_{10}H_{11}N_3O_2$. Calculated % C 58.52; H 5.41; N 20.46

2,5,6-Trimethylpyridine-3,4-dicarboxylic acid N-o-hydroxybenzylidenaminoimide. A mixture of 1.6 g of the N-aminoimide and 1.6 g of salicylaldehyde in alcohol was refluxed for 2 hours. The yield of condensation product was 89-92%; m.p. 191-191.5° (from methanol).

Found %: C 66.17; 66.12; H 4.85; 4.90 $C_{17}H_{15}N_3O_2$. Calculated %: C 66.01; H 4.89.

2,5,6-Trimethylpyridine-3,4-dicarboxylic acid N-p-hydroxybenzylidenaminoimide was obtained in 80% yield; m. p. 233-234.5°.

Found %: C 66.36; H 4.79 $C_{17}H_{15}N_3O_2$. Calculated %: C66.01; H 4.89.

2,5-Dimethylpyridine-3,4-dicarboxylic acid N-aminoimide (IId). The residue obtained after heating 2,5-dimethylpyridine-3,4-dicarboxylic acid with hydrazine was extracted with boiling alcohol. The undissolved material was pyridazinedione Id (0.07 g, 5% yield); m.p. 328-331°. From the alcohol extract was obtained 1.35 g (67.5% of IId; m.p. 175-178°.

Found %: 56.19; 56.01; H 4.69; 4.58 $C_9H_9N_3O_2$. Calculated %: C 56.54; H 4.76

2,5-Dimethylpyrido-(3,4-d)-pyridazinedione (Id). A mixture of 4 g of 2,5-dimethylpyridine-3,4-dicarboxylic acid and 1 g of hydrazine hydrate in 3 ml of glycol was refluxed for 1 hour. The mixture was acidified with dilute acetic acid, and the Id was washed with boiling alcohol. The yield was 2.4 g (60%); m. p. 333° (with decomposition) after distillation under vacuum.

Found %: N 22.30 $C_9H_9N_3O_2$. Calculated % N 21.97

2,6-Dimethylpyrido-(3,4-d)-pyridazinedione (Ib) was obtained in 70% yield by refluxing for 15 minutes a mixture of the acid and hydrazine in glycol; m.p. 290-293° (with decomposition).

Found %: C 55.84; H 4.57 $C_9H_9N_3O_2$. Calculated %: C 56.54; H 4.76

The literature [2] reports an m.p. of 302° (with decomposition).

5,5-Dimethylpyrido-(3,4-d)-pyridazinedione (Ia): 62.5% yield (15-minute heating); m.p. 333° (with decomposition).

Found %: C 55.85; 56.03; H 4.78; 4.91 $C_9H_9N_3O_2$. Calculated %: C 56.54; H 4.76

The yield of Ia from the dimethyl ester of the acid and hydrazine was 89%, while from the dianilide and hydrazine it was 70.2%.

Substance	M.p., °C	Yield, %	Found, %		Calculated, %	
			C	H	C	H
2,5-Dimethylpyridine-3,4-dicarboxylic acid N-phenylimide	133,5—134	51	71,21 71,34	4,72 4,74	71,41	4,79
2,5,6-Trimethylpyridine-3,4-dicarboxylic acid N-phenylimide	152—154	62	72,00 72,16	5,34 5,39	72,17	5,30
2,6-Dimethylpyridine-3,4-dicarboxylic acid N-phenylimide	145—146	52,8	71,12	4,91	71,41	4,79
5,6-Dimethylpyridine-3,4-dicarboxylic acid dianilide	190—192	40	72,88 72,67	5,49 5,40	73,02	5,54

5-Hydroxy-2-methylpyrido-(3,4-d)-pyridazinedione (Ic). The yield was 78% (10-minute refluxing); m.p. 303° (with decomposition).

Found %: C 49.47; 49.60; H 3.89; 3.88 $C_8H_7N_3O_3$. Calculated %: C 49.74; H 3.68

2,5,6-Trimethylpyrido-(3,4-d)-pyridazinedione (Ie). A mixture of 5 g of 2,5,6-trimethylpyridine-3,4-dicarboxylic acid N-phenylimide and 14 g of hydrazine hydrate in 20 ml of glycol was refluxed for 6 hours; the yield of Ie was 73%; m.p. 316° (with decomposition).

Found %: C 58.38; H 5.52; N 20.95 $C_{10}H_{11}N_3O_2$. Calculated %: C 58.52; H 5.41 N 20.48

The yield of Ie from the acid and hydrazine (2-hour refluxing) was 20%, while from the imide of the acid (m.p. 218-220°) and hydrazine it was 65%.

Reaction of pyridine-3,4-dicarboxylic acids with aniline. A mixture of the acid and aniline (1:4) was heated at 160-180° for 2-4 hours, and the resulting precipitate was recrystallized from methanol (see table).

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THE ADDITION OF $HGeCl_3$ TO HALOGEN-SUBSTITUTED ETHYLENE

DEHYDROCHLORINATION OF α, β-DICHLOROETHYLTRICHLOROGERMANE

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In previous work [1] we established that trichlorogermane ($HGeCl_3$), in contrast to trichlorosilane ($HSiCl_3$), adds vigorously at room temperature to various olefins and their derivatives in the absence of a catalyst.

In the present investigation, we studied the addition of $HGeCl_3$ to different chlorine derivatives of ethylene (from $ClCH=CH_2$ to $Cl_2C=CCl_2$), to which it is practically impossible to add $HSiCl_3$. For example, the addition of methyldichlorosilane to vinyl chloride can be accomplished only in an autoclave at 160° in the presence of a catalyst – platinum or carbon [2]. However, the yield of α-chloroethylmethyldichlorosilane under these conditions does not exceed 7% of theoretical.

$$ClCH=CH_2 + HSiCH_3Cl_2 \xrightarrow{Pt/C} CH_3ClCHSiCl_2CH_3.$$

The addition of $HSiCl_3$ and of CH_3Cl_2SiH to dichloroethylene, trichloroethylene, and tetrachloroethylene occurs with still lower yields in spite of the use of initiators and of vigorous conditions [3, 4]. In contrast, as we established in the present investigation, trichlorogermane adds readily to these chlorine derivatives of ethylene in the absence of a catalyst.

For example, when vinyl chloride is bubbled through trichlorogermane, the addition proceeds with the evolution of heat, and this also occurs when trichlorogermane is mixed with dichloroethylene, trichlorethylene, and tetrachloroethylene. It should be remarked that in the latter case the evolution of heat is scarcely noticeable.

However, the most unexpected result was that the interaction of vinyl chloride and trichlorogermane yielded β-chloroethyltrichlorogermane rather than the alpha-substituted compound:

$$ClCH=CH_2 + HGeCl_3 \rightarrow ClCH_2CH_2GeCl_3 \ (33\%)$$

For this reason, we investigated the order of addition of $HSiCl_3$ to vinyl chloride. It was found that, in spite of the use of such an active catalyst as chloroplatinic acid, $HSiCl_3$, as well as CH_3Cl_2SiH, adds to vinyl chloride only in an autoclave and forms α-chloroethyltrichlorosilane in merely 6% yields

$$ClCH=CH_2 + HSiCl_3 \rightarrow Cl_3SiCHClCH_3.$$

It was thus established that trichlorogermane adds to vinyl chloride in a different order than does trichlorosilane, probably owing to different reaction mechanisms for the addition of the two reagents. The cleavage of HCl from α, β-dichloroethyltrichlorogermane was carried out by means of both quinoline and of aluminum chloride.

The use of these two reagents has previously been investigated for a similar cleavage involving the analogous organosilicon compound ($Cl_3SiCHCl \cdot CH_2Cl$) [5, 6].

It was found that in the present case the previously noted regularity was retained; i.e., quinoline split out the β-chlorine atom, and the aluminum chloride split out the α-chlorine atom.

$$Cl_3GeCHClCH_2Cl \xrightarrow{AlCl_3} Cl_3GeCH = CHCl \ (80\ \%)$$

$$Cl_3GeCHClCH_2Cl \xrightarrow[\text{quinoline}]{} Cl_3GeCCl = CH_2 \ (42\ \%).$$

The mechanism of the dehydrochlorination by aluminum chloride has recently been elucidated for α,β-dichloroalkyltrichlorosilanes [7, 8] as a rearrangement of a β-carbonium ion with a shift of the trichlorosilyl group from an alpha carbon to a beta carbon. It is probable that the rearrangement in the present case takes place by this same mechanism:

$$Cl_3GeCHClCH_2Cl \xrightarrow{AlCl_3} \left[Cl_3GeCH\overset{\oplus}{C}H_2 \rightarrow \overset{\oplus}{C}HCH_2GeCl_3\right] \rightarrow Cl_3GeCH = CHCl.$$

An attempt to split out HCl from $Cl_3SiCH_2CHClGeCl_3$ with quinoline led only to β-decomposition:

$$Cl_3SiCH_2\underset{Cl}{C}HGeCl_3 \rightarrow SiCl_4 + CH_2 = CHGeCl_3.$$

The α- and β-chlorovinyltrichlorogermanes possess curious properties. Upon standing for several hours, α-chlorovinyltrichlorogermane spontaneously polymerized to a milky, opaque solid material. As is well known, α-chloro- and α-bromovinyltrichlorosilanes behave analogously [6, 9].

Like its silicon analog [5, 9, 10], when β-chlorovinyltrichlorogermane is titrated with an 0.1 N solution of a base, only three chlorines are hydrolyzed. Thus, we are not dealing here with the expected decomposition with the evolution of acetylene, which is a characteristic of quasicomplex compounds [11] (for example, $Cl_3PbCH = CHCl$ and $Cl_3SnCH = CHCl$). The table presents the properties of five germanium compounds, which were synthesized for the first time in the present work.

EXPERIMENTAL

β-Chloroethyltrichlorogermane, $ClCH_2CH_2GeCl_3$. A stream of vinyl chloride was passed for an hour through 15 g of trichlorogermane [1]. Vigorous evolution of heat occurred at first. The contents of the flask were cooled and then heated on a hot plate at 80° for an hour. A total of 6.5 g of β-chloroethyltrichlorogermane was obtained by vacuum distillation. The compound boiled at 75° (15 mm). The Raman and infrared spectra were in complete agreement with the spectra obtained with β-chloroethyltrichlorogermane previously prepared by a different route [12, 13]. Titration of a sample of β-chloroethyltrichlorogermane in approximately 70% ethanol with 0.1 N NaOH using phenolphthalein indicator led to hydrolysis of precisely four chlorine atoms, but a day was required.

α,β-Dichloroethyltrichlorogermane, $ClCH_2CHClGeCl_3$. To 30 g of trans-dichloroethylene was added, with stirring, 54 g of trichlorogermane at a rate such that the temperature of the liquid did not rise above about 80°. The contents of the flask were then heated for half an hour at 80°, and were then distilled under vacuum. There was obtained 51 g of α,β-dichloroethyltrichlorogermane, b.p. 88° (12 mm). The yield was 62%. Precisely four chlorine atoms were hydrolyzed by 0.1 N base.

Trichloroethyltrichlorogermane, $Cl_3GeC_2H_2Cl_3$. Under the conditions of the preceding experiment, 28 g of trichloroethyltrichlorogermane, b.p. 92° (9 mm), was obtained from 20 g of trichloroethylene and 27 g of trichlorogermane. The yield was 55.3%. Titration with 0.1 N base hydrolyzed four chlorine atoms.

Compound	B.p., °C/mm	Yield, %	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.
$ClCH_2CH_2GeCl_3$ *	75/15	32,5	1,5092	1,7637	41,08	40,35
$ClCH_2 - ClCHGeCl_3$	88/12	62	1,5240	1,8390	46,07	45,20
$Cl_2C_2H_2GeCl_2$	92/9	55,3	1,5341	1,9000	50,95	50,028
$CHCl_2 - CCl_2GeCl_3$	123/25	48	1,5378	1,9243	56,11	54,862
$CH_2 = CClGeCl_3$	151	41,6	1,5002	—	—	—
$CHCl = CHGeCl_3$	164—165	80	1,5139	1,7690	40,92	40,88

* The literature [12, 13] reports a b.p. of 188° (756), $n^{20}D$ 1.5094; d^{20}_4 1.7587.

Tetrachloroethyltrichlorogermane, $Cl_2CHCl_2CGeCl_3$. Twenty grams of tetrachloroethylene and 18 g of trichlorogermane were mixed in a flask at a temperature of 80-90°, and heating was continued for 2 hours after mixing. A total of 16.5 g of tetrachloroethyltrichlorogermane was obtained: b.p. 123° (25 mm). The yield was 48%. A 0.1 N solution of base titrated four atoms of chlorine.

α-Chlorovinyltrichlorogermane, $CH_2 = CClGeCl_3$. A mixture consisting of 27.7 g of α,β-dichloroethyl trichlorogermane and 13 g of quinoline was slowly distilled from a Favorskii flask to an overhead temperature of about 200°. A second distillation of the condensate yielded 10 g of α-chlorovinyltrichlorogermane with a b.p. of 151° (753 mm). The yield was 41.5%. Only three chlorine atoms could be titrated.

β-Chlorovinyltrichlorogermane, $ClCH = CHGeCl_3$. A mixture of 20 g of α,β-dichloroethyltrichlorogermane and 0.2 g of aluminum chloride was slowly distilled from a Favorskii flask. A second distillation yielded 16 g of β-chlorovinyltrichlorogermane with a b.p. of 164-165°. The yield was 80%. Precisely three atoms of chlorine were titrated by 0.1 N base.

β-Chloroethyltrichlorosilane, $CH_2ClCHSiCl_3$. To a glass vessel contained in a 250-ml autoclave were charged 68 g of $HSiCl_3$, 32 g of vinyl chloride, and 0.5 ml of an isopropyl alcohol solution of $H_2[tCl_6 \cdot 6H_2O$ (0.1 N solution). The autoclave was heated at 120° for 4 hours. Distillation yielded 19 g of ethyltrichlorosilane (b.p. 98-103°), the Raman spectrum of which was in complete agreement with the spectrum reported in the literature. The yield was 20% of theoretical. Six grams of a fraction boiling at 136-139° was obtained. The yield was 6%. The Raman spectrum of this fraction correspond to that of α-chloroethyltrichlorosilane; 0.1 N base titrated three chlorine atoms. The ethyltrichlorosilane was apparently formed as a result of the following reactions: $Cl_3SiH + ClCH=CH_2 \rightarrow$ $\rightarrow Cl_4Si + CH_2=CH_2$; $CH_2=CH_2 + HSiCl_3 \rightarrow C_2H_5SiCl_3$. The spectra were taken by L. A. Leites.

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THE POLAROGRAPHIC DETERMINATION OF MICRO AMOUNTS OF METALS USING A STATIONARY MERCURY DROP AS AN ELECTRODE

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In connection with the necessity of developing a polarographic analytical method of increased sensitivity, there has arisen a new branch – oscillographic polarography – which has increased the sensitivity of the method by one to two orders of magnitude. However, the possibilities of increasing the sensitivity of the ordinary method of polarographic analysis still have not been exhausted. A good prospect in this regard is the use of catalytic currents [1] as well as new electrodes (the rotating mercury drop [2], stationary mercury electrodes [3], and various solid electrodes [4]). The highest sensitivity can be attained through the use of stationary spherical mercury electrodes of small surface, if electrolysis is first carried out at constant potential in order to deposit ions in the mercury with the formation of an amalgam (to concentrate the elements); this is followed by anodic solution of the metals using an ordinary polarograph to record the curves. Most of the work in which stationary electrodes, "hanging" or "lying" drops have been used, have been carried out with an oscillographic polarograph. Kemula and Kublik [5] used for this purpose an ordinary polarograph and a "hanging" mercury drop as the electrode, and they showed that it is possible to detect certain metal impurities in reagents at concentrations down to 10^{-8} M. However, these authors did not carry out systematic quantitative investigations.

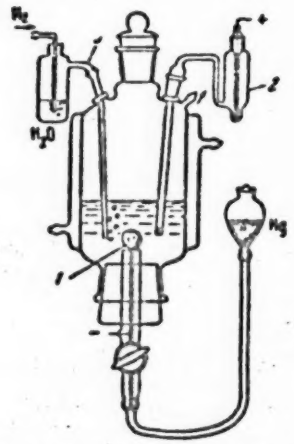

Fig. 1. Electrolytic cell. 1) Electrode with "lying" drop; 2) saturated calomel electrode; 3) nitrogen inlet.

The present article shows that through the use of preliminary enrichment of the stationary mercury drop, it is possible to carry out quantitative determinations of a number of elements which form amalgams (Cu, Cd, In, Pb, Zn, etc.) by means of anodic solution curves; these determinations may be made at concentrations of the metal in the solution down to 10^{-8} M. In order to establish optimum conditions for carrying out the analysis, systematic investigations were carried out on the effects of various factors (size of drop surface, electrolysis time for enrichment, rate of stirring of the solution, temperature, etc.) on anode current values during solution of the metals. A modification of the cell of Nikelly and Cooke [6] was used; this is shown in Fig. 1. The primary electrode was a drop of mercury "lying" on a capillary; the drop was formed by turning the stopcock a specified number of times. The capillary was first covered with a film of chlorosilane. The other electrode was a saturated calomel electrode, the end of which dipped into the solution close to the mercury drop. Stirring of the solution during the preliminary electrolysis was accomplished by means of a stream of nitrogen, which was passed into the solution at a controlled rate.

Some 20-40 ml of carefully prepurified electrolyte (0.2 M KCl, KNO_3, HCl) was placed in the electrolytic cell, and the solution of the

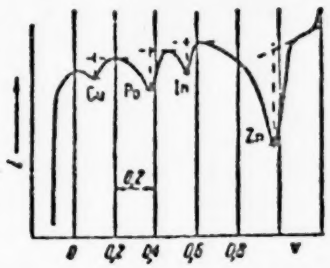

Fig. 2. Anode solution curves for solution of metals from amalgams. Concentrations: Zn 0.01 γ/ml ($1.6 \cdot 10^{-7}$ M), In 0.005 γ/ml ($4.5 \cdot 10^{-8}$ M), Pb 0.01 γ/ml ($5 \cdot 10^{-8}$ M), Cu 0.01 γ/ml ($1.7 \cdot 10^{-7}$ M).

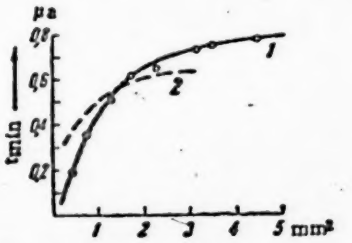

Fig. 3. Relationship between current minimum for anode solution of lead and surface area of the mercury drop (C_{Pb} = 0.1 γ/ml). 1) With capillary covered with a chlorosilane film; 2) capillary not covered.

ion being investigated was added in a volume such that the concentration of the ion was 10^{-3} M; stirring of the solution by means of the nitrogen stream was then initiated. The slide wire was then adjusted so as to give a potential 0.2-0.3 volts more negative than the half-wave potential of the ion being determined, both electrodes were connected to the polarograph, and the timer was simultaneously switched on. Electrolysis was carried out over a fixed period of time (10-30 minutes), and a minute prior to completion of the electrolysis the stream of nitrogen was stopped (the Hg drop then came to a quiescent state). Upon completion of the electrolysis, a curve was obtained for anodic solution of the metal from the amalgam with the polarograph operating in reverse, i.e., from a more negative to a more positive potential. The anode solution curves presented in Fig. 2 were obtained in this manner. The position along the potential axis of the current minima of these curves identifies the metal, and the magnitude of the minimum determines the concentration of the metal in the amalgam. This same figure shows the graphic method used for measuring the current minima.

Through a study of the analysis of a very dilute lead solution (0.1γ/ml) it was established that the surface area of the mercury drop (Fig. 3), the rate of stirring, the electrolysis time, and the temperature all have a great effect on the magnitude of the current minimum of lead. However, when these conditions are maintained constant, it is possible to obtain readily reproducible results. As our experiments showed, the best conditions for analysis are: a drop diameter of 1.3-1.6 mm, a stirring rate of not less than that produced by a pressure of 80 m.m of water *, and an electrolysis time of 10-30 minutes. An increase in temperature increases the sensitivity of the method. (The temperature coefficient of the current was 3% in the temperature range 20-60°.) Under standard experimental conditions, the relationship between the value of the current minimum and the concentration of the metal was linear for a number of elements (Pb, Cu, In, Zn) over a concentration interval of 10^{-7} to 10^{-3} M (Fig. 4), which indicates that the proposed method of analysis is reliable.

The value of the current minimum is determined by two processes: the rate of deposit of the metal ions in the stationary mercury cathode and the rate of anode solution of the metal from the amalgam. The first process depends on the rate of convective diffusion of the ions to the surface of the drop, and diffusion layer theory may be applied to the process. It can be described by the equation

$$C = C_0 e^{\frac{-ADt}{VS}}, \qquad (1)$$

where C_0 is the initial concentration of the ions (in g-ions/mole); C is the ion concentration at time t in a volume V (ml) with a cathode surface of A (cm^2); D is the diffusion coefficient (cm^2/sec); S is the thickness of the diffusion layer (cm).

Equation (1) may be written in the form:

$$t = \frac{2{,}303\,VS}{AD} \log \frac{C_0}{C} = \frac{2{,}303\,VS}{AD} \log \frac{I_0}{I}. \qquad (2)$$

* Internal diameter of the tube was 3.5 mm.

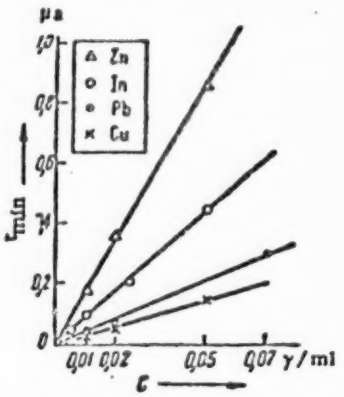

Fig. 4. Dependence of anode current during solution of metals on concentration of ions in the solution.

Equation (2) permits calculation of the time required for complete deposition of the metals in the mercury. However, in contrast to the method of Hickling and co-workers [7] who used a stationary mercury electrode with a large surface (1 cm^2) and quantitative deposition of the metals in the mercury, the method proposed by us for concentration of the elements in the amalgam does not require their quantitative deposition. It is only necessary that when the stirring rate and other conditions are maintained constant, the amount of metal deposited be a linear function of its concentration in the solution for a fixed electrolysis time and a linear function of electrolysis time for a fixed concentration of the element. As may be seen from our results (Fig. 4), the required linear relationship is quite satisfactorily followed.

The second process – anode solution of the metal – is determined chiefly by the rate of diffusion of the metal in the mercury to the mercury – electrolyte boundary and also by the surface area of the amalgam, the temperature, and other factors [8]. Our results on the current values during anodic solution of lead, cadmium, indium, and zinc correlate well with the value of the diffusion coefficients of these metals in mercury [9] and also with their solubilities in mercury [10]. The very low values of the current during anodic solution of copper cannot be explained solely by the low value of its diffusion coefficient in mercury ($D = \sim 1.0 \cdot 10^{-5}$ $cm^2 \cdot sec^{-1}$) nor by the low solubility of copper in mercury (0.003%); apparently, copper forms a series of compounds with mercury which, in the opinion of Russel et al. [11], may have a composition from Cu_7Hg to $CuHg_4$. Moreover, the possibility of the formation of intermetallic compounds during solution of two or more metals in mercury cannot be excluded. However, this phenomenon has no effect on the quantitative determination of these metals, though the sensitivity of the method for copper is lower. The presence of surface-active substances (gelatin and others) in the solution has an appreciable effect on the value of the current, which is decreased by these substances. For example, the current minimum for lead is decreased by 16% when $1 \cdot 10^{-3}$% gelatin is present in the solution.

An important advantage of the proposed method is that it is possible to determine several elements in one solution, since neither elements which dissolve from the amalgam at more negative potentials nor elements which dissolve at more positive potentials (even when their content is ten-fold and more that of the metal being determined) have an effect on the value of the current minimum. This circumstance makes our proposed method very suitable for the simultaneous quantitative determination of several impurities. When impurities are determined from the anode solution curves by the method of reference [7], only one metal can be determined, because only the first metal dissolving from the amalgam gives the correct value of the limiting current, and metals subsequently dissolving at more positive potentials yield current values which are too low; in the opinion of the authors, this is the result of an electrochemical substitution reaction.

Our investigation also showed that it is possible to carry out repeated determinations of the ions using the same solution, provided the mercury drop is renewed each time. This permits the use of the addition method for quantitative determination of elements. Another important advantage of the method is that it is possible to determine very small amounts of impurities when there is present in the solution a large excess of ions with a more negative reduction potential (for example, indium may be determined in a concentration of 0.05 γ/ml with an In : Co ratio of $1 : 10^5$). In order to accomplish this, it is necessary to carry out the electrolysis for indium enrichment at a more positive potential than the reduction potential of cobalt (at −0.9 volt relative to the normal calomel electrode). In this case, the measured current minimum for the anodic solution of indium is the same as its value in the absence of cobalt. The average relative error of the proposed method for a metal concentration of $10^{-7} - 10^{-8}$ M does not exceed ± 6%. The maximum deviation is ± 15%.

The authors express their appreciation to Corresponding Member of the Academy of Sciences USSR L. P. Alimarin for valuable advice during the progress of the work.

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AN INVESTIGATION IN THE FIELD OF BORON COMPOUNDS

OXIDATIVE POLYMERIZATION OF TRIALLYLBORON

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The introduction of hetero atoms into hydrocarbon polymer chains leads to the formation of polymers with new and valuable properties. There is a large number of well-known low molecular weight esters of boric acid as well as different polymers of thioboranes, aminoboranes, phosphinoboranes, polyorganoborosiloxanes, etc. Goubeau and Apple [1], in a study of the thermal decomposition of trimethylboron at 400-600°, showed that, along with hydrogen and methane, there are formed solid products of various colors from light yellow to black, all of which contain boron. The interaction of ethynylmagnesium bromide with boron trifluoride etherate in benzene yields the magnesium salt of tetraphenylethynylboric acid, which undergoes decomposition and polymerization when heated under vacuum [2]. Among the different pyrolysis products of $(CH_3)_2BCH_2CH_2B(CH_3)_2$ are nonvolatile polymeric boron-containing compounds [3]. Kolesnikov and Fedorova [4] showed that tributylboron in the presence of boron trifluoride etherate causes polymerization of acrylonitrile. It was found that tributylboron is an active catalyst for the polymerization of styrene and methyl methacrylate.

TABLE 1

Polymers Obtained by Oxidation of Triallylboron (elemental compositions are in percent)

Oxidation conditions	B	C	H	O	M.p., °C
Unpurified O_2-containing nitrogen (0.8%)	4,31	57,27	8,30	29,52	>250
In tert-butylbenzene at 130° ($N_2 + O_2$)	5,03	60,04	9,09	25,84	>250
In isopropylbenzene at 130° ($N_2 + O_2$)	4,38	61,55	9,19	24,88	>250
Benzoyl peroxide at 20° (1 : 1)	4,33	57,24	8,89	29,54	>250
H_2O_2 at 20° (1 : 1)	4,26	56,02	9,24	30,48	>250

The purpose of the present investigation was to study the polymers obtained from triallylboron [5] and to show that it is a catalyst for the polymerization of unsaturated hydrocarbons.

EXPERIMENTAL

Solid yellowish polymers, together with triallylboron, are formed when triallylboron is prepared in a stream of nitrogen not sufficiently freed from oxygen. Elemental analysis confirmed the presence of boron and oxygen in

TABLE 2

Fractions of Polymers Obtained by Oxidation of Triallylboron (elemental compositions in percent)

Experimental conditions	Fraction	B	C	H	O	Cl
Heated to 75°, 1.5 hours, in CCl_4	Insoluble	6.79	21.22	5.05	55.75	10.19
	Soluble	3.13	63.84	9.18	20.48	3.37
Heated to 65°, 1.5 hours, in tetrahydrofuran	Insoluble	11.71	23.90	5.01	59.38	–
	Soluble	3.72	62.99	9.98	23.71	–
Stood in 10% KOH at 20° for several days	Insoluble	4.59	54.26	9.30	31.85	–
	Soluble	5.49	58.98	9.39	26.15	–

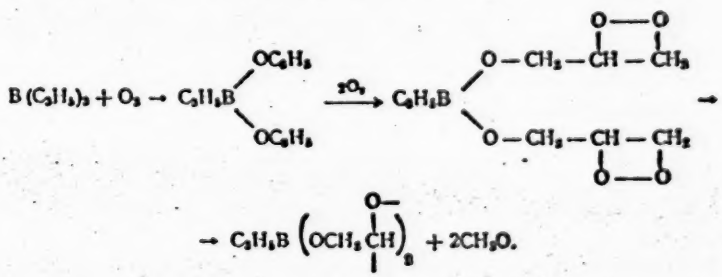
these polymers (Table 1). We carried out systematic experiments on the polymerization of triallylboron with atmospheric oxygen and also in solution in isopropylbenzene and tert-butylbenzene at 130° with a nitrogen – oxygen mixture. The elemental composition and melting point were determined for the polymers obtained in these experiments.

No polymer was obtained when the attempted polymerization of triallylboron with 5 mole % benzoyl peroxide added was carried out in sealed tubes from which the atmospheric oxygen had been purged with nitrogen; the experiments were carried out at 100°. Polymer was obtained when benzoyl peroxide was added to the triallylboron in mole ratios of 1:1 and higher. The reaction was very violent with considerable evolution of heat. The benzoyl peroxide decomposed according to the scheme

$$C_6H_5CO-O-O-COC_6H_5 \rightarrow (C_6H_5CO)_2O + O^{\cdot}.$$

The same reaction takes place with hydrogen peroxide.

Thus, triallylboron is a compound which is readily polymerized in the presence of oxygen. In order to elucidate the reaction mechanism involved in the polymerization, triallylboron was subjected to oxidation with a mixture of nitrogen and oxygen. The gas leaving the flask with the oxidized sample gave a well-defined aldehyde reaction: The sample acquired a lilac-blue color when fuchsin sulfurous acid was added, and the solution was acidified with hydrochloric acid; not only the first portions of gas, but those sampled during the course of the experiment gave this test. The polymerization may be represented as follows:



The active chains arising as a consequence of the decomposition can react either among themselves or by addition to unoxidized triallylboron molecules at the site of the double bond, forming trimeric products in both cases. A scheme for oxidative polymerization was proposed by Danilov and Koz'mina [6], who, during an investigation of allylcellulose, came to the conclusion that this ether can polymerize through the allyl groups by a reaction in which oxygen participates.

This scheme has been completely confirmed by our investigations. As is well known, trimeric polymers are insoluble, nonswelling, infusible products, and this was confirmed by the properties of the polymers studied in the present investigation. They were difficultly soluble in various solvents. Soluble and insoluble fractions were formed

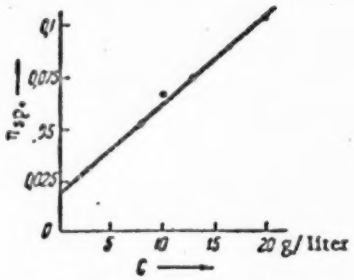


Fig. 1. Dependence of relative* viscosity of polymethyl methacrylate on concentration.

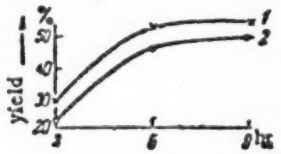


Fig. 2. Kinetics of the polymerization of styrene at 100° in the presence of triallylboron: 1) without $B(C_3H_5)_3$; 2) with 5 mole % $B(C_3H_5)_3$.

by prolonged treatment of the polymer with 10 percent KOH, and the first fraction was separated from the alkaline solution by the addition to the solution of dilute hydrochloric or nitric acid. When the polymer was heated at 65-75° in carbon tetrachloride or tetrahydrofuran for 1.5 hours, soluble and insoluble fractions were obtained. The solvent was removed from the soluble fraction by evaporation. All of the CCl_4-soluble polymer can be converted to insoluble polymer by this method. The polymer behaved similarly with tetrahydrofuran. Moreover, it is interesting that the elemental analyses showed that the chlorine content of the CCl_4-insoluble polymer (10.19%) was higher than that of the soluble fraction (3.37%), and the oxygen content of the polymer insoluble in tetrahydrofuran and in the base was higher than that of the soluble polymer (Table 2). The melting points of these polymers were above 250°. It was not possible to determine the molecular weights of these polymers owing to their poor solubility.

We also studied the ability of triallylboron to cause or inhibit polymerization reactions of a number of vinyl compounds. All experiments were carried out in sealed tubes from which air was purged from the gas phase by means of nitrogen. The tubes were held at 100°; 5 mole % triallylboron was added.

Triallylboron was an active catalyst for the polymerization of methyl methacrylate. The reaction proceeded with considerable evolution of heat, and after 1-1.5 hours reaction at room temperature, the methyl methacrylate had become a solid, transparent block. Polymer yield was up to 86%. No boron was found during the determination of the elemental composition (Table 3), which indicates that triallyboron

TABLE 3

Substance	Experimental conditions	Yield of polymer, %	Observed changes	Found %		
				B	C	H
Styrene	3 hr, 100°	29.26	Transparent viscous liquid	—	92.21	7.79
Styrene + 5 mole % $B(C_3H_5)_3$	3 hr, 100°	23.36	Same	—	92.31	7.74
Styrene	6 hr, 100°	51.23	Same	—	92.25	7.80
Styrene + 5 mole % $B(C_3H_5)_3$	6 hr, 100°	44.48	Same	—	92.20	7.80
Styrene	9 hr, 100°	52.04	Transparent block	—	92.31	7.70
Styrene + 5 mole % $B(C_3H_5)_3$	9 hr, 100°	48.81	Same	—	92.35	7.67
Methyl methacrylate + 5 mole % $B(C_3H_5)_3$	1-1.5 hr, 20°	84.3	Same	—	60.70	8.25
Acrylonitrile + 5 mole % $B(C_3H_5)_3$	70 hr, 100°	—	No change	—		
Vinyl acetate + 5 mole % $B(C_3H_5)_3$	50 hr, 100°	—	No change			

does not copolymerize with the methyl methacrylate. The dependence of the viscosity of the polymethyl methacrylate on concentration is shown in Fig. 1. Triallyboron had no noticeable effect on the polymerization of styrene. It only very slightly inhibited the polymerization process. Thus, tubes containing styrene were held at 100° for 3, 6, and 9 hours; triallylboron was added to some of the tubes and omitted from others.

* Stated to be specific on the ordinate—Translator.

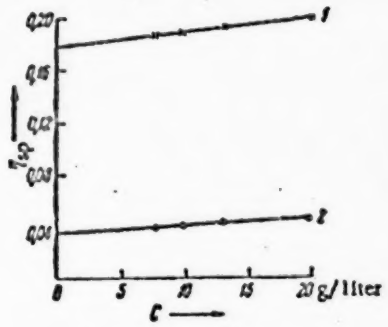


Fig. 3. Dependence of the relative viscosity of polystyrene on concentration: 1) without $B(C_3H_5)_3$; 2) with $B(C_3H_5)_3$.

The yields of polymer were, respectively: without the addition of $B(C_3H_5)_3$, 29.26, 51.23, 52.04%; with the addition of 5 mole % $B(C_3H_5)_3$, 23.36, 44.48, 48.81%. The variation in polymer yield with polymerization time is shown in Fig. 2. The viscosity of polystyrene prepared in the presence of triallylboron was significantly lower (Fig. 3).

We also studied the polymerization of acrylonitrile and of vinyl acetate in the presence of 5 mole % triallylboron. Triallylboron did not bring about polymerization of these compounds, even when the tubes were held at 100° for prolonged periods (50 to 75 hours). Data obtained in our study of the polymerization of a number of unsaturated compounds are presented in Table 3.

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* Original Russian pagination. See C. B. Translation

HYDROGENATION OF FURAN COMPOUNDS OVER SKELETAL Cu – Al CATALYST

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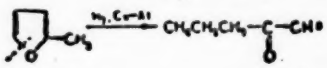
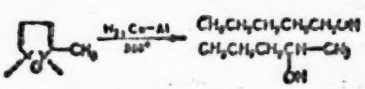
Copper catalysts, particularly copper chromite, have been quite widely used for the hydrogenation of furan compounds. The ability of these catalysts to hydrogenate double bonds and carbonyl groups without affecting the furan ring permits their use for the selective reduction of furan compounds containing various unsaturated bonds in the molecule. The useful sphere of copper catalysts in the hydrogenation of compounds of the furan series is limited chiefly by the necessity of carrying out the reaction under liquid-phase conditions. Furfural, sylvan, furyl alcohol, furfurylidene ketones, and many other furan compounds are either reduced over copper chromite to more saturated furan compounds or are converted to aliphatic alcohols or diols as a result of hydrogenolysis of the ring. Moreover, in contrast to certain other catalysts, for example, Adams platinum catalyst, hydrogenolysis of the ring in sylvan and in furyl alcohol over copper chromite proceeds in both possible directions – at both the 1,2 and 1,5 C–O bond [1]. However, vapor-phase hydrogenation of sylvan at ordinary pressure and 275° over copper chromite [2], and also over skeletal Cu–Al [3], results in opening of the ring at only one site, namely, at the 1,5 CO bond. All of these facts suggest an investigation of the effect of pressure and temperature on the succession in which unsaturated bonds are reduced in various compounds of the furan series. The effect of these factors on the hydrogenation of furan compounds over skeletal Cu – Al catalyst was investigated in the present work.

1. The investigation showed that pressure exerts a decisive effect on the direction of hydrogenolysis of the furan ring. As is well known, when sylvan is subjected to hydrogenolysis over skeletal Cu–Al in a flow system at normal pressures, the ring is opened exclusively at the C–O bond not adjacent to the methyl group, which leads to the formation of methyl propyl ketone [3]:

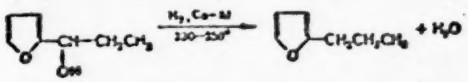


If, however, the hydrogenation of sylvan is carried out in the vapor phase but at elevated hydrogen pressure, the furan ring is cleaved at both possible locations–at the 1,2 and 1,5 C–O bonds–and the relative amounts of the resulting alcohols, 1-pentanol and 2-pentanol, vary appreciably depending on the hydrogen pressure used. Thus, at 250° and 50 atm hydrogen pressure, 41% 1-pentanol and 44% 2-pentanol were formed, while at 25 atm and the same temperature, 33% 1-pentanol and 54% 2-pentanol are formed:

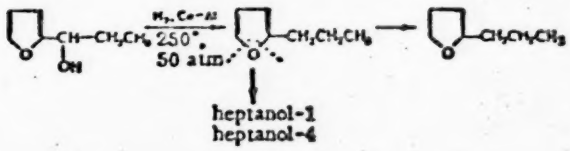


An increase in temperature favors, on the one hand, dehydrogenation of the 2-pentanol to methyl propyl ketone and, on the other hand, deeper decomposition of the sylvan with the formation of n-pentane and water. About 30% n-pentane, 12% methyl propyl ketone, 20% 1-pentanol, and 24% 2-pentanol were formed at 340-350° and 50 atm. Moreover, hydrogenation of sylvan at elevated hydrogen pressure gave in all cases tetrahydrosylvan in a yield of 5-8%. As is well known, tetrahydrosylvan is not formed in the presence of this catalyst at normal pressure.

2. When alkylfurylcarbinols are hydrogenated over skeletal Cu—Al catalyst at either ordinary or elevated hydrogen pressure, the primary reaction is hydrogenation of the hydroxyl group and conversion of the alkylfurylcarbinol to the corresponding α-alkylfuran. At ordinary pressure and 230-250°, α-alkylfurans can be obtained in yields of up to 95%:

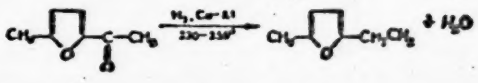


Subsequent hydrogenolysis of the ring, which becomes more extensive at higher temperatures, leads to the formation of aliphatic ketones. However, the high degree of selectivity with respect to hydrogenation of the hydroxyl group and retention of the furan ring is not observed when the hydrogenation is carried out under elevated hydrogen pressure. Under these conditions, hydrogenolysis of the ring proceeds more vigorously and in two directions, and the reaction products contain, along with α-alkylfurans, aliphatic alcohols and a small amount of α-alkyltetrahydrofurans. For example, the hydrogenation of ethyl-α-furylcarbinol in a flow system at 250° and 50 atm hydrogen pressure gave 22% α-n-propylfuran, 10% α-n-propyltetrahydrofuran, 24% 1-heptanol, and 25% 4-heptanol:

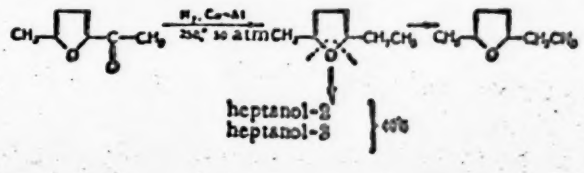


3. As in the case of alkyl- α-furylcarbinols, it is possible for the primary reaction in the vapor-phase hydrogenation of alkyl α-furyl ketones to be reduction of the carbonyl group with retention of the furan ring. Nickel deposited on zinc or cadmium oxide [4], for example, is a catalyst for this reaction, but another sequence of reactions—reduction of the carbonyl group and hydrogenolysis of the furan ring—is also possible. Thus, when the reaction is carried out in the vapor phase and at ordinary pressure over platinized carbon, hydrogenolysis of the furan ring at the C—O bond adjacent the carbonyl group in α-methyl-α'-acetylfuran takes place before reduction of the carbonyl group, and the primary hydrogenolysis products undergo further conversion with the formation of oxygen-containing carboxylic compounds with six-membered rings [5].

In the hydrogenation of alkyl furyl ketones in the vapor phase at ordinary pressure, skeletal Cu—Al catalyst behaves similarly to nickel catalysts, i.e., the carbonyl group is reduced first without touching the furan ring, and this catalyst is distinguished by its higher selectivity. For example, when 2-methyl-5-acetylfuran was hydrogenated at 230-250°, the yield of 2-methyl-5-ethylfuran was 90-95%:



Here, as in the case of alkylfurylcarbinols, the use of elevated hydrogen pressure sharply decreased the selectivity of reduction of the carbonyl group, since it promoted hydrogenolysis of the furan ring to a very considerable extent:

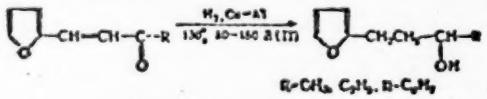


Properties of the Furan Alcohols and Spiranes Prepared in the Present Work

Hydrogenation product	B.p., °C	d_4^{20}	n_D^{20}
1-α-Furyl-3-butanol	67—69 (4)	1,0202	1,4754
1-α-Furyl-3-pentanol	77—78 (4)	1,0023	1,4750
1-α-Furyl-3-hexanol	97—98 (5)	0,9861	1,4707
1-α-Furyl-2-methyl-3-pentanol *	84—85 (5)	0,9928	1,4738
2-Methyl-3-α-furyl-1-propanol	72—74 (4)	1,0243	1,4785
2-Ethyl-3-α-furyl-1-propanol	80—83 (3)	1,0059	1,4797
2-iso-Propyl-3-α-furyl-1-propanol	97—100 (4)	1,0013	1,4846
3-Methyl-1,6-dioxaspiro-(4,4)-nonane	58,5—60 (15)	0,9966	1,4452
3-Ethyl-1,6-dioxaspiro-(4,4)-nonane	49—50,5 (4)	0,9788	1,4489

* In Doklady Akad. Nauk SSSR 128, 946 (1959), through an oversight the authors erroneously gave for this compound the constants of 1-(α-furyl)-2-methyl-1-penten-3-one.

4. Skeletal Cu—Al catalyst displayed high activity and selectivity for the liquid-phase reduction of furfurylidene ketones and α-alkyl-β-furylacroleins to the corresponding furan alcohols. At 120-140° the yield of 1-α-furyl-3-alkanols was 90-95%, and the yield of 2-alkyl-3-α-furyl-1-propanols was 75-85%.



R=CH₃, C₂H₅, n-C₃H₇

R=CH₃, C₂H₅, i-C₃H₇

3-Methyl-1,6-dioxaspiro-(4,4)-nonane and 3-ethyl-1,6-dioxaspiro-(4,4)-nonane were isolated in yields of 12-20% from the hydrogenation products of α-alkyl-β-furylacroleins. The physical properties of the furan alcohols and spiranes obtained in the course of the work are presented in the table (for literature values, see the article by A. Ponomarev [6]).

Thus, the results of the present investigation show that the use of elevated pressure during the hydrogenation of α-alkylfurans over skeletal Cu—Al in a flow system results in hydrogenolysis of the furan ring in two directions with the formation of primary and secondary aliphatic alcohols. Normal pressure is the best condition for the selective hydrogenation of alkylfurylcarbinols and alkyl furyl ketones to the corresponding α-alkylfurans when the reaction is carried out in a flow system over skeletal Cu—Al catalyst. Skeletal Cu—Al has a higher selectivity than copper chromite for the liquid-phase hydrogenation of furfurylidene ketones and α-alkyl-β-furylacroleins to the corresponding furan alcohols.

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THE ELECTRONIC STRUCTURE OF CHROMOCENE AND CERTAIN OTHER RELATED COMPOUNDS

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(Presented by Academician L. L. Chernyaev, October 31, 1959)

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In previous work [1]* we have carried out molecular orbital (m. o.) calculations for dibenzenechromium, ferrocene, and the cobalticinium cation (by the method of Roothaan [2]), which were consistent among themselves. According to these calculations, both in ferrocene and in dibenzenechromium, there is a certain effective positive charge on the central atom such that the electrons are partially shifted from the central metal atom to the aromatic ring. This result is contrary to the concept accepted by certain authors that donor–acceptor bonds between pairs of π electrons of the aromatic ligands and free orbitals of the central atoms play a decisive role in the stability of aromatic complexes of metals [3], since such bonds would have to lead to transfer of electrons from the ring to the metal atom. The electron density distribution found by us indicates that in dibenzenechromium the reverse shift of electrons, which corresponds to the formation of a dative type bond (formed by a pair of electrons from the metal and free antibonding orbitals of the ring), compensates and even outweighs the shift due to donor – acceptor bonds. The positive charge on the metal atom in ferrocene is less than in dibenzenechromium, since in the first of these molecules, donor – acceptor bonds lead to a greater shift of electrons from the ring to the Fe, and this shift cannot be compensated by dative bonds and is outweighed only by the high polarity of the e_{1g} type bonds (due to unpaired electrons of C_5H_5 and Fe) with a shift of electrons from the Fe to the ring.

Symmetry	Bonding m.o.		Antibonding m.o.
	orbital	energy, ev	energy, ev
a_{1g}	$0{,}97a_{1g} + 0{,}25s$	—13,71	+1,74
a_{1g}	d_{z^2}	—4,82	—
a_{1u}	$0{,}99a_{1u} + 0{,}06p_z$	—13,12	+3,73
e_{1g}	$0{,}92e_{1g} + 0{,}39d_{xz}$	—10,56	+7,04
e_{1u}	$0{,}94e_{1u} + 0{,}35p_x$	—9,82	+4,05
e_{2g}	$0{,}55e_{2g} + 0{,}83d_{xy}$	—5,22	+5,88
e_{2u}	—		+4,00

It seems to us that these results may be connected with the relative distribution of the atomic orbitals of the central atom and of the m.o. of the ring, since conditions for the interaction of a.o. and m.o. of the same symmetry depend on the differences in the energies of corresponding orbitals. A rough idea of the distribution of a.o. may be obtained from atomic spectra. Corresponding schemes for Fe and Cr are presented in Fig. 1. These diagrams show that the levels of a free Cr atom lie above the corresponding levels of an Fe atom. On the one hand, the a and e levels of the π electrons of the C_5H_5 ring, both bonding and antibonding, are lower than the corresponding levels of the C_6H_6 ring (see Fig. 2). Therefore, it may be assumed that conditions for interaction with the formation

* There is an error in our previous article [1]; all values of dipole moments, both those in the tables and those in the text, should be multiplied by 4.8.

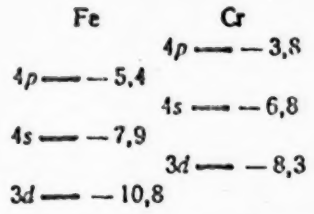

Fig. 1. Location of atomic electron levels in Fe and Cr atoms (in ev).

of donor — acceptor bonds are less favorable in dibenzenechromium, since the occupied orbitals in C_6H_6 are low and the free Cr orbitals are comparatively high, so that the corresponding bonds would probably be weak. The dative bonds should be stable, because the occupied de_{2g} orbitals of the Cr and the free e_{2g} orbitals of the ring are of close to the same energy (see Fig. 3). On the other hand, in the case of ferrocene the distance between the lowest-lying free a.o. of the Fe and the highest π orbitals of the C_5H_5 should be less than in dibenzenechromium, since an increase in the role of donor — acceptor bonds would be expected owing to the less favorable conditions for dative interaction in ferrocene. In connection with the above, it would appear interesting to consider the chromocene molecule, $(C_5H_5)_2Cr$, which has the same central atom as dibenzene chromium and the same ligands as ferrocene and which, therefore should be intermediate between $(C_5H_5)_2Fe$ and $(C_6H_6)_2Cr$.

In the present work, we carried out m.o. calculations for chromocene using the method of Roothaan in its generalized form for radicals [4] [since $(C_5H_5)_2Cr$ has two unpaired electrons]. During the course of the calculations, some simplifying assumptions were made, similar to those made in our previous work [1]. The molecular orbitals and their energies are shown in the table. The ground state of $(C_5H_5)_2Cr$ has the form

$$(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(e_{2g})^2(a_{1g})^1. \qquad (A)$$

Another possible triplet state is

$$(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a_{1g})^2(e_{2g})^2, \qquad (B)$$

in which both unpaired electrons occupy the doubly degenerate e_{2g} level, which lies above the a'_{1g} level, which, in turn, is occupied by a pair of electrons; we reject this state because we were unable to obtain self-consistent m.o. This conclusion as to the ground state is in agreement with our previous conclusion arrived at on the basis of a consideration of the valence state of chromium in chromocene [5]. The calculated energy levels e_{2g} and a'_{1g} are close together, so that the diamagnetic state

$$(e_{2g})^4(a'_{1g})^0. \qquad (C)$$

lies close to the ground state.

This shows that the observed paramagnetism of chromocene and the absence of an equilibrium between the para- and diamagnetic forms is due not to a significant difference in the energies of the upper occupied electronic levels, but to a difference in the energies of the original valence states leading to molecular states A and B (128 and 187 kcal, respectively).

The latter conclusion relates not only to $(C_5H_5)_2Cr$, but apparently, also to other aromatic complexes. In all of the molecules which we have considered, the upper occupied levels are levels of symmetry e_{2g} and a'_{1g}, and these levels are of closely similar energy. Moreover, in $(C_5H_5)_2Fe$ and $(C_5H_5)_2Co^+$, the e_{2g} level lies above the a'_{1g} level, while there is an inversion in the case of the Cr compound (probably owing to the greater role of dative bonds), and the e_{2g} level is below the a'_{1g} level. Apparently, the a_{1g} and e_{2g} levels are almost accidently degenerate in aromatic metal complexes. This conclusion as to the symmetry of the upper occupied levels and their quasi-degeneracy is confirmed by the experimental data of McConnell [6] on the paramagnetic resonance of vanadicene, $(C_5H_5)_2V$, for which he found that the three unpaired electrons are distributed between the $(e_{2g})^3$ and $(a'_{1g})^1$ levels.*

The presence of three close energy levels (two e_{2g} levels and an a'_{1g} level) leads to the conclusion that from the point of view of m.o. energy, the difference between states with different distributions of electrons between the

* According to the calculations of Yamazaki [7], the upper occupied level of $(C_5H_5)_2Fe$ has the symmetry e_{1u}. This seems improbable to us in the light of our valence state and m.o. calculations and of the experimental data on the paramagnetic resonance of vanadicene.

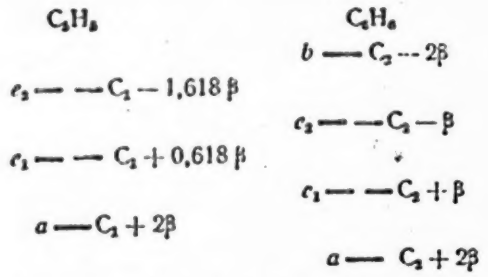

Fig. 2. Distribution of π-electron levels in C_5H_5 and C_6H_6 rings by the simple m.o. – l. c. a. o. method ($C_2 < C_1$)

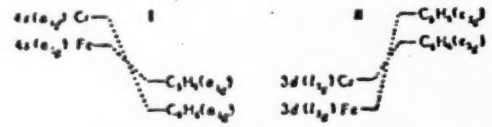

Fig. 3. Relative distribution of orbitals participating in the formation of a_{1g} (I) type donor–acceptor bonds and e_{2g} (II) type dative bonds.

a'_{1g} and e_{2g} levels should be small. This confirms our previous conclusion that the number of unpaired electrons in aromatic complexes is determined by the energy difference between the initial valence states.

The ionization potential of chromocene (the energy of the upper occupied level a'_{1g}) is 4.82 ev, which is 70% of the experimental value (6.90 ev).

The a.o. and m.o. coefficients of chromocene lead to the following charge distribution: +1.70 electronic charge on the Cr atom and −0.17 on each C atom. Thus, the charge on the Cr atom is significantly greater than that on the Fe atom in $(C_5H_5)_2Fe$ (+0.68). This result is in agreement with the substantial difference in the properties of ferrocene and chromocene. It is well known from chemical data that $(C_5H_5)_2Cr$ differs greatly from typically covalent biscyclopentadienyl compounds, approaching the ion $Mn^{2+}(C_5H_5^-)_2$, which appears momentarily in the metathetical reaction with $FeCl_2$ (with a ferrocene yield of 70%), in acid hydrolysis, and in electrical conductivity measurements [8]. A study of infrared spectra led to this same conclusion – that $(C_5H_5)_2Cr$ is significantly ionic and that it is closely similar to $(C_5H_5)_2Mn$. On the other hand, the charge on the Cr atom in $(C_6H_6)_2Cr$ is close to that found for $(C_6H_6)_2Cr$ (+1.47), which is in agreement with the small dipole moment of the mixed complex $(C_6H_6)Cr(C_5H_5)$ (between 0 and 0.4 D) [10]. That the charges on the Cr in the dibenzene and biscyclopentadienyl compounds are almost the same, together with the appreciable ionic character of $(C_5H_5)_2Cr$, suggests that $(C_6H_6)_2Cr$ must be a partially ionic molecule in which the benzene rings play the part of the anions (in the same way that they act as anions in interactions with alkali metals).

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THE CIS-ISOMER OF THE INNER-COMPLEX SALT FORMED BY DIVALENT PLATINUM AND α-ALANINE

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(Presented by Academician A. A. Grinberg, November 21, 1959)

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Inner-complex salts of the general formula $[PtA_2]$*, which are prepared by the reaction

$$K_2PtCl_4 + 2AH \rightarrow [PtA_2] + 2KCl + 2HCl. \quad (1)$$

should exist in the form of two geometric (cis- and trans-) isomers. In 1931 A. A. Grinberg and V. V. Ptitsyn [1] showed that in the case of GlH, reaction (1) leads to both isomers of $[PtGl_2]$ in a molecular ratio of cis- to trans- of about 3:1. It was shown in 1934 [2] that the reaction of K_2PtCl_4 with excess of GlH neutralized with a base proceeds according to the equation:

$$K_2PtCl_4 + 4GlH + 4KOH \rightarrow K_2[PtGl_4] + 4KCl + 4H_2O. \quad (2)$$

The addition of the calculated amount of acid to the soluble salt $K_2[PtGl_4]$ gave the difficultly soluble compound H_2PtGl_4:

$$K_2[PtGl_4] + 2HCl \rightarrow H_2PtGl_4 + 2KCl, \quad (3)$$

It has also been shown [3] that when H_2PtGl_4 is heated with water, it is converted to the cis-isomer of the inner-complex salt**:

$$H_2PtGl_4 \rightarrow 2GlH + \text{cis-}[PtGl_2]. \quad (4)$$

In 1937, one of us, together with A. A. Grinberg [4], showed that in the case of AnH (in contrast to the case of GlH), reaction (1) leads to the formation of only the trans-isomer of $[PtAn_2]$. In the interaction of K_2PtCl_4 with an excess of AnH neutralized with base, the reaction proceeds according to an equation similar to (2); however, the compound H_2PtAn_4 is not precipitated by the addition of an acid to the salt $K_2[PtAn_4]$ (the presence in the solution of $[PtAn_4]^{2-}$ anions was demonstrated [4] by isolation of the compound $[Pt(AnH)_4Cl_2]Cl_2$, which was formed from the $[PtAn_2]^{2-}$ by oxidation of Pt(II) to Pt(IV) in an acid medium). Cis-$[PtAn_2]$ not only was not detected among the products of reaction (1), but it could not be prepared by a reaction similar to (4), since the compound H_2PtAn_4 was not isolated.

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* AH is generic notation for monobasic amino acids; GlH represents α-aminoacetic acid (glycine); AnH represents α-aminopropionic acid (alanine); and BH represents α-aminobutyric acid.

** It has recently been established that this reaction proceeds in two stages; the compound $HPtGl_3$ is formed in the first stage.

In 1957, both isomers of the inner-complex salt $[PtB_2]$ were synthesized by one of us [5]. However, in the case of BH (as in the case of AnH) reaction (1) led to the formation of only the trans-$[PtB_2]$. Cis-$[PtB_2]$ was synthesized from the compound $K_2[PtB_4]$, which in turn was synthesized by reactions similar to (2), (3), and (4). We may remark that, as was shown by the work reported in reference [6], a reaction of the type of (2) provides a general method for the preparation of $K_2[PtA_4]$ compounds. Thus, only in the case of AnH (of the three simplest members of the α-amino acid homologous series) does the cis-isomer of the inner-complex salt still remain unknown. The proposal that there is some hindrance (steric, for example) which interferes with the formation of cis-$[PtAn_2]$ has become improbable since the synthesis of the cis-isomers of $[PtGl_2]$ and $[PtB_2]$. Therefore, we considered that it was of major importance to attempt again the synthesis of this isomer.

EXPERIMENTAL

As was noted above, the compound H_2PtAn_4 did not precipitate when acid was added to a solution of $K_2[PtAn_4]$. However, the compound H_2PtAn_4 had to be present in the solution, and we assume that by heating the solution (by analogy to the behavior of H_2PtGl_4 and H_2PtB_4 which separated in solid form), the H_2PtAn_4 would be converted to cis-$[PtAn_2]$. An experiment confirmed this assumption.

To 5 mmoles of K_2PtCl_4 were added 20 mmoles each of AnH and KOH; the total volume of the solution was about 20 ml. The solution was heated for 1 hour on a water bath. To the almost colorless solution was added 1 M HCl (calculated on the basis of 2 mmoles of HCl per mmole of original K_2PtCl_4), and the mixture was heated for 2-3 hours on a water bath, during which time the volume of the solution was maintained constant at 12-15 ml. When the solution was cooled, a voluminous white precipitate formed; this was suction filtered, washed with water, alcohol, and ether, and dried at 105°. The precipitate was found to be pure $[PtAn_2]$ (about 30% yield).

Found %: Pt 52.55; 52.59; 52.63; N 7.62; 7.72 $[PtAn_2]$. Calculated %: Pt 52.57; N 7.54

The properties of preparations of $[PtAn_2]$, obtained by the route described above, differed considerably from the properties of preparations (identical in composition) of trans-$[PtAn_2]$ prepared by reaction (1) [4]. The solubility of cis-$[PtAn_2]$ in water (1.1% at 25°) was about 14 times greater than the solubility of the trans-isomer. The trans-isomer formed tabular crystals, while the cis-isomer formed rods. The isomers differed particularly in their behavior toward hydrochloric acid. When concentrated HCl was added to the cis-isomer, even in the cold, there was instantaneous and complete disappearance of the original precipitate, and a bright-yellow solution was obtained; under the same treatment, the trans-isomer became slightly yellow, but did not go into solution. Upon warming, the cis-isomer dissolved in just the theoretical amount of 1 M HCl (2 moles of HCl per mole of cis-$[PtAn_2]$).

The trans-dichloride $[Pt(AnH)_2Cl_2]$ has previously been obtained [4] from trans-$[PtAn_2]$ by refluxing with an excess of concentrated HCl (10 ml per g of the inner-complex salt). For the preparation of the cis-dichloride, we added 2 ml of concentrated HCl to 1 g of cis-$[PtAn_2]$, and the reaction mixture was heated for less than one minute on a water bath. A yellow precipitate of the cis-dichloride formed when the mixture was cooled; the precipitate was transferred to a glass filter using concentrated HCl as the transfer medium, and it was then washed with ether and dried at 100°.

Found %: Pt 43.63; 43.76; N 6.22; 6.17 $[Pt(AnH)_2Cl_2]$. Calculated %: Pt 43.94; N 6.30

The yield of the cis-dichloride was 80%. The alanine rings opened when the isomeric inner-complex salts were treated with HCl: $[PtAn_2] + 2HCl \rightarrow [Pt(AnH)_2Cl_2]$.

Both dichlorides are dibasic acids, and they may be quantitatively titrated with a base in the presence of phenolphthalein; the products of the reaction $[Pt(AnH)_2Cl_2] + 2KOH \rightarrow [PtAn_2] + 2KCl + 2H_2O$ are isomeric inner-complex salts.

The isomeric dichlorides have considerably different properties. The cis-dichloride is considerably more soluble in water than the trans-isomer (both are difficultly soluble in concentrated HCl); on the contrary, the trans-dichloride dissolves considerably more readily in ether than does the cis-dichloride.

The isomers differ with respect to their behavior toward thiourea (Thio) and other reagents. When acted upon by thiourea (under identical conditions), the cis-dichloride gives about an 80% yield of a yellow precipitate of $[Pt(Thio)_4]Cl_2$ (found: Pt 34.29 and 34.02%; calculated: 34.21%), while the trans-dichloride gave a white precipitate of $[Pt(Thio)_2(AnH)_2]Cl_2$ [4].

The absence of the cis-isomer of $[PtAn_2]$ from the products of reaction (1) is quite natural, since free HCl was found in the solution, in the presence of which cis-$[PtAn_2]$ is very readily converted to the soluble cis-dichloride.

These same results were obtained when K_2PtCl_4 was reacted with BH; the solubilities of cis-[$PtAn_2$] and cis-[PtB_2] in water [5] were almost equal. Cis-[$PtGl_2$] was appreciably less soluble in water (0.18% at 25°) than was its analog; therefore, it was prepared, though in low yield, by the interaction of K_2PtCl_4 with GlH.

Thus, the cis- and trans-isomers of [PtA_2] have now been prepared for all three of the simplest α-amino acids.

In conclusion, we may note that the compound H_2PtAn_4, from which we assume we prepared cis-[$PtAn_2$], has recently been isolated by us (though in low yield), and it will be reported on later.

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MOLECULAR COMPOUNDS OF CHLOROPHYLL WITH CERTAIN METALS

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There is a considerable amount of data showing that it is possible for chlorophyll to form molecular complexes with polar compounds [1-6]. Some authors have proposed [4] that the cyclopentadiene ring, which is active in a number of chemical reactions, is responsible for the formation of these molecular compounds. Others [1-3] have proposed that the polar molecules add at the central, magnesium atom. It might be supposed that an important role in the formation of addition products is also played by the nitrogen atoms of the pyrrole rings, which are centers of localization of electron density in the chlorophyll molecule. This is suggested by data recently obtained in our laboratory [7-8], which showed that chlorophyll a forms molecular complexes with such electrophylic reagents as ferric chloride and stannic chloride.

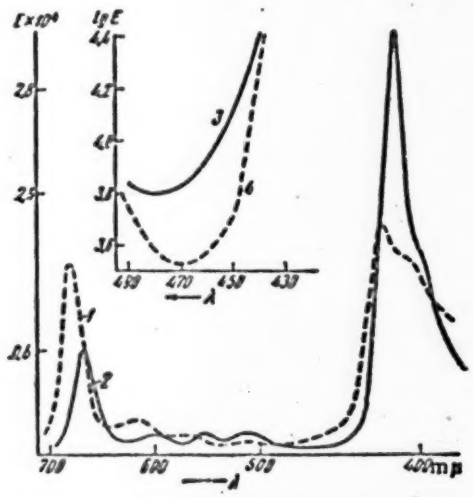

Fig. 1. Changes in the absorption spectrum of an acetone solution of chlorophyll a during interaction of the latter compound with $AgClO_4$. 1) Spectrum of the original solution of chlorophyll a; 2) the same after the introduction of $AgClO_4$; 3) spectrum of the molecular complex of chlorophyll with $AgClO_4$ in the λ 440-490 mμ region; 4) spectrum of the molecular complex pheophytin a with $AgClO_4$ in the λ 440-490 mμ region.

The data presented in the present article show that similar compounds with chlorophyll (and pheophytin) are also formed by other chlorides — $HgCl_2$, $BeCl_2$, $AlCl_3$, $BiCl_3$, and $NbCl_5$ — and also by silver perchlorate. These compounds can be isolated in the solid state. Analyses carried out on the solid complex of chlorophyll with ferric chloride showed that the components are present in a 1:1 ratio.

The interaction of any of these salts with chlorophyll leads to deformation of the absorption spectrum of the pigment. These spectroscopic changes are illustrated in Fig. 1 for the case of the interaction of chlorophyll with $AgClO_4$ in acetone. It may be seen from Fig. 1 that the spectrum retains, for the most part, the structure characteristic of dihydroporphyrins. The number of bands and their relative distribution is the same as for chlorophyll; however, their absolute position is different. The two most intense chlorophyll bands are shifted considerably toward the short-wave region. The sharp decrease of the red band and the strong increase in the intensity of the Soret band are conspicuous. Within the

TABLE 1

	I		II		III		IV		V	
	λ, mμ	ε·10⁻⁴	λ, mμ	ε·10⁻⁴	λ, mμ	ε·10⁻⁴	λ, mμ	ε·10⁻⁴	λ, mμ	ε·10⁻⁴
Chlorophyll	663	13,9	617	2,76	580	1,59	535	0,92	430	17,3
$AgClO_4$·Chl	553	7,85	600	1,61	565	1,51	532	1,66	418	32,0
$SnCl_2$·Chl	553	7,06	600	1,82	565	1,80	532	1,94	418	30,0

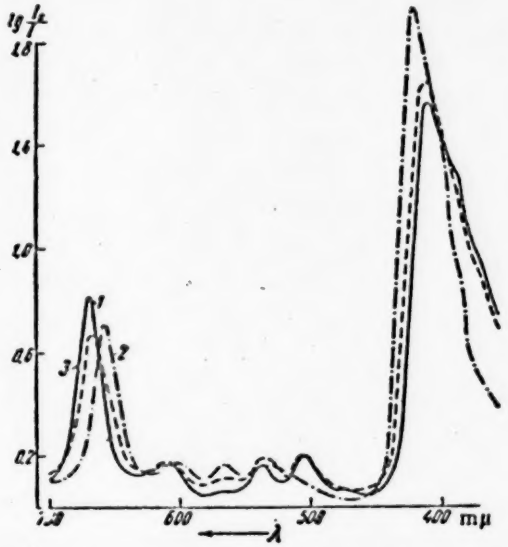

Fig. 2. Curves showing the reversibility of the molecular interaction of pheophytin with water. 1) Absorption curve of the original solution of pheophytin a; 2) the same after the introduction of $SnCl_2$; 3) the same after the addition of 2% water.

limits of error of the measurements, the spectra of the molecular complexes formed by the chlorides enumerated above differ little among themselves and from the spectrum presented in Fig. 1 (curve 2). A characteristic feature of these spectroscopic changes is that they may be detected in the presence of small amounts of the salts in solution. Thus, when chlorophyll a (in a concentration of the order of 10^{-5} mole/liter) is reacted with silver perchlorate (in a concentration of not less than $1 \cdot 10^{-4}$ mole/liter), the equilibrium is shifted completely in the direction of the formation of the molecular complex. At lower salt concentrations, the solution contains both chlorophyll and molecular complex. This makes it possible to determine the absorption coefficient at the maximums in the spectra of the molecular compounds studied in the present work. We assumed, moreover, that one molecule of chlorophyll enters into the composition of each molecule of complex.* Table 1 presents such data for molecular compounds of chlorophyll with silver perchlorate and with stannous chloride. It may be seen from the data of Table 1 that the absorption coefficients of these two compounds differ little from each other. The good reproducibility of the values obtained in a series of repetitions of the measurements should be noted.

The absorption spectra of the products of the interaction of pheophytin with the same salts were very close to those just discussed. It should be noted, however, that the absorption of the "chlorophyll product" in the 440-500 mμ region was strong in comparison with the absorption of the "pheophytin product", as shown by the curves in the upper left-hand corner of Fig. 1. This would appear to be a small difference in the spectra; however, it showed up very clearly in the color of the solutions of the corresponding products: The "chlorophyll product" was green, and the "pheophytin product" had a pale blue tint.

The addition of these same salts to chlorophyll b and pheophytin b also produced changes in the spectra.

The above-described changes in the spectra of chlorophyll and pheophytin are observed not only in acetone, but also in other solvents (methanol, ethanol, benzene, benzyl alcohol, etc.) The fact that no deviations from the Lambert-Beer law were observed upon considerable dilution indicates that these complexes are quite stable. It is characteristic, however, that in the presence of a very small amount of moisture, decomposition of the complex takes place with the regeneration of the original pigment. This reverse process is quite clearly observable when

* This assumption was subsequently confirmed by analytical data.

TABLE 2

Positions of the Absorption Bands of Pheophytin b and Its Complex with $HgCl_2$ in Acetone

	Wave length of absorption maximums, mμ				
	I	II	III	IV	V
Pheophytin b	660	605	–	530	428
Molecular complex of pheophytin b with $HgCl_2$	651	590	555	525	423

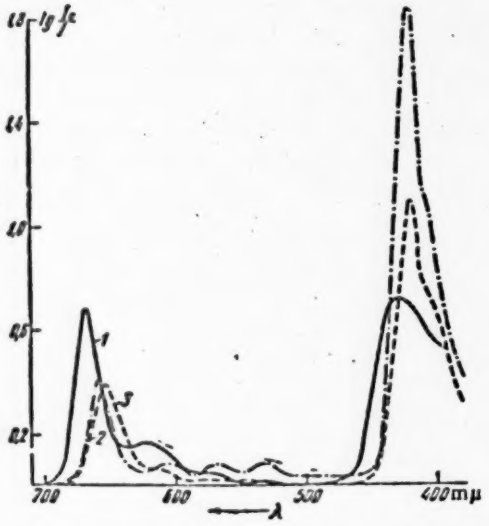

Fig. 3. Changes in the spectrum of a methanol solution of chlorophyll during the course of the reaction with $AgClO_4$. 1) Absorption curve for the original solution; 2) the same immediately after the introduction of the $AgClO_4$; 3) the same after the solution had stood in the presence of $AgClO_4$ for three days.

traces of moisture are added to the appropriate solution (Fig. 2). The high sensitivity of the reaction of the pigment with the salt to traces of moisture imposes rather strict requirements on the conditions under which the experiments are carried out: It is necessary to use anhydrous salts and solvents which have been dried to as great an extent as possible, and the experiments must be carried out under conditions such that penetration of atmospheric moisture into the reaction sphere is prevented. The majority of the experiments were carried out under vacuum, by the method described in reference [7].

If the experiments on the effect of moisture indicate that the interaction of chlorophyll with salts is reversible, then the behavior of these solutions during prolonged storage under vacuum indicates the occurence in these solutions of irreversible processes in which the metal of the salt is substituted for the central atom in the pigment molecule. Figure 3 illustrates a process of this type in the case of the interaction of chlorophyll a with $AgClO_4$.* Processes analogous to this transformation of pheophytin by the complexing salts have been previously observed during the interaction of chlorophyll a with ferric chloride and with stannous chloride [7, 8]. This thus confirms our previously published idea that the formation of molecular complexes of chlorophyll with salts is an intermediate stage in processes in which the central atom of a pigment is replaced and that it takes place prior to the replacement of the central atom. In its general form, this process can be described as follows: $MgPh + MCl_2 \rightleftarrows MgPh \cdot MCl_2 \rightarrow MPh + MgCl_2$.

The first stage of the process is rapid and occurs immediately after the components are mixed. The rate of the second stage depends on the natures of the reacting salts and the solvent. Thus, replacement of Mg by Hg or Be takes place over a period of a few minutes. With Fe, Sn, and Ag, this process requires days. The introduction of Bi and Al ions into the chlorophyll nucleus has not been demonstrated at all. Such processes proceed more rapidly in methanol than in acetone, and they do not occur at all in benzene solutions. According to our data, the electrical properties of the solvent and the magnitudes of the effective radii of the corresponding ions play an essential role in the second stage of the process.

*The spectrum of the final product (curve 3, Fig. 3) was identical to the spectrum of silver pheophytin, which was previously obtained in our laboratory by M. S. Ashkinazi and V. E. Karpit-ska.

As noted above, the interaction of chlorophyll with salts in benzene solution is accompanied by the same changes in spectra which characterized the reaction in acetone solution. However, the solubility of the resulting primary reaction products in this nonpolar solvent is very low, and they rapidly and completely precipitate. This feature of benzene solutions was used for the separation of the molecular compounds in the pure form and for the qualitative and quantitative determination of their compositions. Although the separation of the complexes as solids was demonstrated during the interaction of the pigments with the majority of the salts used, it was nevertheless possible to obtain a product suitable for analysis only in the case of the reaction of chlorophyll (and pheophytin) with $FeCl_3$. In the remaining cases, the problem was complicated by the difficulty of washing the products free of excess salt.

The carefully purified product of the interaction of these pigments with $FeCl_3$ was a blue powder. It was completely insoluble in benzene, ether, and acetone, in which the free pigments are readily soluble. However, it was quite readily soluble in slightly acidified acetone and in a mixture of benzene and acetone (1:5).

In the determination of the composition of the complex, four parallel experiments gave the following molar ratios of chlorophyll to $FeCl_3$: 1:1.02, 1:1.5, 1:1.1, and 1:1.13. The following ratios were obtained for the complex of pheophytin with $FeCl_3$: 1:0.94, 1:0.88 (in three experiments), and 1:0.85. On the basis of these results, we assume that the molecular ratio of pigment to $FeCl_3$ in these interaction products is 1:1.

With respect to the question of the nature of the bonds of these metal salts with the chlorophyll in the molecular complexes, only a preliminary opinion may be indicated. It is most probable that the molecule of salt (the electrophilic reagent) adds to the chlorophyll at one of the nitrogen atoms of the pyrrole rings, and that one of the unshared electron pairs is used for the bond. This is particularly indicated by the fact that the bonds between the Mg and the nitrogen atoms in the resulting compound are weakened, which is the cause of the easy replacement of the magnesium atom by the metal of the added salt. The addition of salt molecules to chlorophyll must be inevitably lead to the "jump" of an electron inside the molecular compound, and consequently to a redistribution of the electron density in the conjugated system of π bonds in the porphyrin skeleton. The experimentally observed changes in the spectrum during the formation of the molecular complex are connected with this. The addition of the molecule of salt does not directly affect the conjugated system: The effect is an inductive one through the nitrogen atoms, which, it may be assumed, explains why the observed changes in the spectra were insignificant and why the spectra of complexes with different metals are closely similar in structure in the visible region.

The authors take this opportunity to express their deep appreciation to B. Ya. Dain for guidance during the course of the work.

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A NEW TRITERPENE – MYRICOLAL

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(Presented by Academician B. A. Arbuzov, September 28, 1959)

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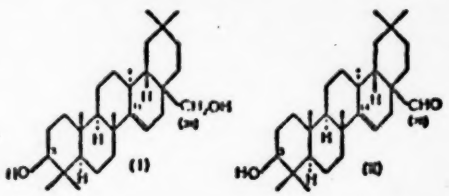
We previously isolated from the roots of Myrica gale L. the triterpene myricadiol, and showed that it is taraxer-14-ene-3β,28-diol (I).

The present communication presents the results of an investigation of another triterpene extracted from the same plant material, which we have chosen to call myricolal. This triterpene has the molecular formula $C_{30}H_{48}O_2$, and forms an acetate and a 2,4-dinitrophenylhydrazone; the absorption spectrum of myricolal has a band at 3553 cm^{-1}, which indicates the presence of a hydroxyl group. When oxidized with chromium trioxide, myricolal is converted to taraxer-14-en-3-one-28-al (myriconal), a substance which we previously obtained by oxidation of myricadiol under analogous conditions. Therefore, the structure of myricolal must correspond to the compound



(I) (II)

taraxer-14-en-3-ol-28-al or taraxer 14-en-28-ol-3-one. In the spectrum of myriconal we found two absorption bands, one at 1709 cm^{-1} (ketone group), and one at 1725 cm^{-1} (aldehyde group), while in the spectrum of myricolal there was only one of these bands, the one at 1726 cm^{-1}, which corresponds to an aldehyde group. Thus, myricolal is taraxer-14-en-3-ol-28-al. The steric configuration of the hydroxyl at the third carbon atom remained unknown. In order to answer this question, we reduced myricolal with lithium aluminum hydride. This resulted in myricadiol, the diacetate of which was identified by comparison with the diacetate of natural myricadiol. Consequently, the configurations of the secondary hydroxyls in myricadiol and myricolal are the same.

The material presented above proves the structure of myricolal to be that of taraxer-14-en-3β-ol-28-al (II).

EXPERIMENTAL

Isolation of Myricolal. The acetone mother liquors remaining after the separation of myricadiol were evaporated, and the tarry residue was dissolved in benzene. An equal volume of a 20% solution of KOH in methanol was added, and the mixture was refluxed for 3 hours. Water was then added, and the benzene layer was separated and evaporated to dryness. The residue was extracted several times with small portions of boiling acetone. The insoluble portion was recrystallized from a mixture of alcohol and dioxane. This yielded 350 mg of crystals with an m.p. of 285° (corrected).

Found %: C 81.55; H 10.90 $C_{32}H_{52}O_3$. Calculated %: C 81.76; H 10.98

Application of the usual methods gave the acetate which, after recrystallization from a mixture of alcohol and dioxane, melted at 304-305°; the 2,4-dinitrophenylhydrazone melted at 250°.

Reduction of Myricolal. To a solution of 100 mg of myricolal in a mixture of 3 ml of ether and 3 ml of benzene was added 3 ml of a 2 N solution of lithium aluminum hydride, and the mixture was refluxed for 3 hours. Further treatment was in the usual manner. An attempt to recrystallize the substance from dioxane led to the formation of a gel, which is characteristic of myricadiol; therefore, the substance was acetylated. After two recrystallizations from a mixture of alcohol and chloroform, the acetate melted at 252-254°. A mixture of this material with myricadiol diacetate melted at 254-255°.

The microanalyses were carried out by E. A. Sokolova, and L. D. Shishkina carried out the spectroscopic investigations. Student V. Tikhonov participated in the work.

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* See C. B. translation.

THE PREPARATION OF DIBORANE BY REDUCTION OF BORON TRIFLUORIDE ETHERATE WITH CALCIUM HYDRIDE

V. I. Mikheeva, E. M. Fedneva, and V. I. Alpatova

(Presented by Academician L. L. Chernyaev, November 10, 1959)

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The reduction of halogen compounds of boron by calcium hydride has not been extensively studied.

According to Hurd [1], when boron trichloride vapors are heated in the presence of hydrogen at a temperature above 200°, gaseous products containing diborane are formed. Hagenmüller and de Pape [2] studied the interaction of gaseous boron trifluoride with calcium hydride and found that diborane is formed at 225-300°, but the reaction is not complete at this temperature. At 300-700°, the major reaction products are higher boranes and boron, while calcium boride, CaB_6, is the major product at higher temperatures. These authors considered the reduction of boron trifluoride by calcium hydride to be a new method for the preparation of boron (at 300°) and calcium boride (at 700°).

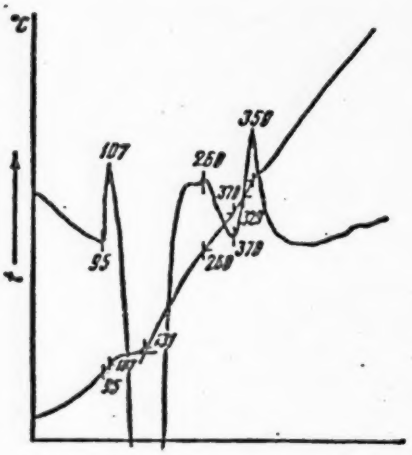

Fig. 1. Thermogram of a mixture of calcium hydride and boron trifluoride etherate.

The present work was devoted to the problem of finding conditions under which the reduction of boron trifluoride etherate by calcium hydride would yield diborane, and it was a continuation of our work on the reaction of boron trifluoride with lithium hydride [3-5]. In investigating the reaction of BF_3 etherate with calcium hydride, a thermographic study of this reaction was first carried out using a Kurnakov pyrometer connected to record temperature differentials; samples of the effluent gas were taken during the thermal analysis and were analyzed.

The thermal analysis showed that evolution of diborane practically coincided with the beginning of boiling of the boron trifluoride etherate (120°), and the greatest amount was obtained at a mole ratio of CaH_2 to BF_3 of close to 3:2; the reaction probably proceeded according to the equation

In addition to the thermal effect corresponding to this reaction (which was maximized by superposition of the heat of vaporization of the boiling etherate), all thermograms (Fig. 1) showed an endothermic effect at 250-322°, which corresponded to decomposition of calcium fluoborate, $Ca(BF_4)_2$, (decomposition temperature 260-295° [6]: $Ca(BF_4)_2 \rightarrow$ $\rightarrow CaF_2 + 2BF_3$, and an exothermic effect at 300-333° due to the formation of elemental boron according to the equation:

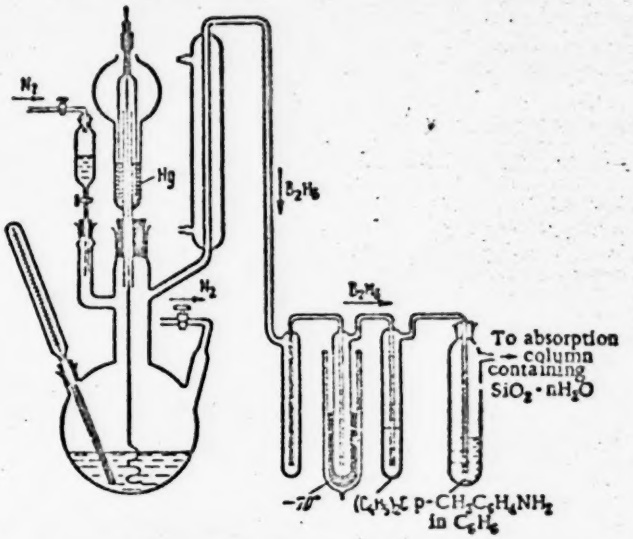

Fig. 2. Apparatus for the preparation of diborane.

Synthesis of diborane was carried out at a temperature close to the boiling point of the etherate. The apparatus consisted of a reactor fitted with a mechanical stirrer with a mercury seal, a reflux condenser, a dropping funnel, an inlet tube for nitrogen, and a thermometer (Fig. 2). The calcium hydride (150 mesh) was charged to the reactor, and the boron trifluoride etherate was added gradually. Vigorous evolution of diborane began when the mixture was heated to 110-120°, and the diborane was absorbed in a benzene solution of para-toluidene. The yield of diborane was calculated in two ways: from the amount combined with the amine and from the consumption of calcium hydride.

The ratio of the reactants had a decisive effect on the yield of diborane (table). When the amount of boron trifluoride etherate was insufficient, a spontaneous exothermic reaction developed in the reaction mixture approximately one to two hours after evolution of the diborane had begun. This resulted in an increase in the temperature of the mixture to 450-500°. When this occurred, the reaction mixture darkened, and the yield of diborane dropped sharply (experiments 1 and 2). The highest yield was obtained with an excess of etherate of up to 60% (experiments 4 and 6). Elemental bromine and iodine had no activating effect on this reaction.

CaF_2, $Ca(BF_4)_2$, CaH_2, and elemental boron were found in the solid reaction product by x-ray (Debye) and chemical methods. The presence of $Ca(BF_4)_2$ was confirmed by thermal analysis. The formation of calcium fluoborate can be represented by the scheme: $CaF_2 + 2BF_3 \rightarrow Ca(BF_4)_2$.

Chemical methods failed to disclose the presence of calcium fluoborate in the reaction products. The diborane was identified as its p-toluidine and trimethylamine addition products, which were identified by boron content, hydride hydrogen content, and melting point.

Found % B 8.98; 9.12; $H_{hydr.}$ 2.47; 2.39 $CH_3C_6H_4NH_2 \cdot BH_3$. Calculated % B 8.95; $H_{hydr.}$ 2.489 M.p. 59-60° (literature [7]: 60°).

Found % B 14.95; 14.70; $H_{hydr.}$ 4.130; 4.125 $(CH_3)_3N \cdot BH_3$. Calculated % B 14.83; $H_{hydr.}$ 4.128 M.p. (after distillation) 94° (literature [8]: 94°).

The results of our work show that diborane can be obtained in good yield by reduction of boron trifluoride etherate with calcium hydride.

Data from the Study of the Reaction of Calcium Hydride with Boron Trifluoride Etherate

Expt. No.	Charged, g (mole)		Mole ratio	B_2H_6 yield, %		$p\text{-}CH_3C_6H_4NH_2 \cdot BH_3$			Reaction temp., °C
	CaH_2	$BF_3 \cdot (C_2H_5)_2O$	$CaH_2 : BF_3$	by CaH_2 consumpt.	by amt. $CH_3C_6H_4-NH_2 \cdot BH_3$	g	m.p., °C	hydr. content, %	
1	12,6 (0,3)	35,5 (0,25)	3 : 2,5	22	Not det.	—	—	—	120°, then to 450°
2	13,6 (0,32)	35,5 (0,25)	3,2 : 2,5	62	Not det.	—	—	—	the same
3	10,22 (0,25)	32,7 (0,23)	1 : 1	20	Not det.	—	—	—	the same
4	4,2 (0,1)	14,3 (0,1)	1 : 1	≈100	Not det.	—	—	—	120°
5	6,32 (0,15)	14,2 (0,1)	3 : 2	73	65	20,61	58—60	2,47	120°
6	6,33 (0,15)	21,3 (0,15)	1 : 1	≈100	95	22,45	58—59	2,39	the same
7	6,32 (0,15)	35,3 (0,15)	3 : 5	75	70	30,60	58—59	2,28	the same

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CONTRIBUTION TO THE PROBLEM OF THE MECHANISM OF THE ADDITION OF SILICON HYDRIDES TO UNSATURATED COMPOUNDS IN THE PRESENCE OF PLATINIZED CHARCOAL AND CHLOROPLATINIC ACID

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The researches of Benkeser and Hickner [1], Speier and coworkers [2, 3], and Goodman, Silverstein and Benitez [4] on the mechanism of the addition of silicon hydrides to unsaturated compounds in the presence of platinized charcoal and of chloroplatinic acid have indicated that the addition proceeds by a heterolytic ionic mechanism.

Our observations on the "concurrent" addition of fluoroethyl allyl ethers led us to the contrary conclusion that the reaction instead proceeds by a specific homolytic reaction [5, 6]. Its specificity is due to the occurrence of the reaction on the surface of a heterogeneous catalyst. The possibility of radical reactions of a similar type being catalyzed by a heterogeneous catalyst has recently been placed on a theoretical [7, 8] and experimental basis [9].

In the present work, we proposed to study the mechanism of the addition of silicon hydrides to unsaturated compounds in the presence of platinized charcoal. We first of all attempted to "fix" the radicals appearing during the interaction of silicon hydrides with platinized charcoal and obviously bound to the catalyst, using diphenylpicrylhydrazyl for this purpose. The data shown in Table 1 persuasively indicate that the catalyst significantly facilitated the homolytic rupture of the Si—H bond in $C_6H_5SiH_3$, $(C_6H_5)_2SiH_2$, $(C_6H_5)_3SiH$, $(C_2H_5)_3SiH$, and $CH_3(C_2H_5)_2SiH$, leading to the formation of atomic hydrogen, which was "fixed" by the diphenylpicrylhydrazyl.

$$\equiv Si-H \xrightarrow[\sim 80-85^\circ]{Pt/C} \equiv \dot{S}i + \dot{H} \xrightarrow{(C_6H_5)_2\dot{N}C_6H_2(NO_2)_3} \equiv \dot{S}i + (C_6H_5)_2NNHC_6H_2(NO_2)_3.$$

That this reaction was not accompanied by hydrogenation of the NO_2 group was shown by the reverse conversion of diphenylpicrylhydrazine to the diphenylpicrylhydrazyl free radical, which was readily accomplished under the influence of lead peroxide

$$(C_6H_5)_2NNHC_6H_2(NO_2)_3 \xrightarrow{PbO_2} (C_6H_5)_2N\dot{N}C_6H_2(NO_2)_3.$$

As may be seen from Table 1, the rate at which the Si—H bonds were ruptured depended essentially on the structure of the silicon hydride: The more the reacting Si—H bond was protected by the substituents, the more difficult bond rupture took place. In the case of $(C_6H_5)_3SiH$, almost no homolytic hydrogenation of the diphenylpicrylhydrazyl occurred under our standard conditions. Neither toluene nor tetrafluoroethyl allyl ether, either in the presence or absence of the catalyst, formed radicals which could be "captured" by the diphenylpicrylhydrazyl.

TABLE 1

Homolytic Hydrogenation of Diphenylpicrylhydrazyl (I)

Expt. No.	Silicon hydride	Amount, moles	Amount of I, g	Amount of 1% Pt/C, g	Times for conversion of I to II, min
1	$CH_3(C_2H_5)SiH$	2.04 (0.02)	0.0050	—	240* **
		2.04 (0.02)	0.0050	0.0200	180*
2	$(C_2H_5)_2SiH$	2.32 (0.02)	0.0050	—	100
		2.32 (0.02)	0.0050	0.0200	40
3	$C_6H_5SiH_3$	2.16 (0.02)	0.0050	—	40
		2.16 (0.02)	0.0050	0.0200	2
4	$(C_6H_5)_2SiH_2$	3.70 (0.02)	0.0050	—	20
		3.70 (0.02)	0.0050	0.0200	10
5	$(C_6H_5)_3SiH$	2.50 (0.01)	0.0025	—	240**
		2.50 (0.01)	0.0025	0.0100	240**
6	$CH_2=CHCH_2OCF_2CFClH$	3.49 (0.02)	0.0050	—	240**
		3.49 (0.02)	0.0050	0.0200	240**
7	$C_6H_5CH_3$	1.85 (0.02)	0.0050	—	960**
		1.85 (0.02)	0.0050	0.0200	960**

* At the boiling point of the hydride, 78°.

** Appreciable change of I was not observed over the time interval indicated.

As we have previously reported [6] with respect to "concurrent" addition the silicon hydrides investigated may be arranged in the following order of decreasing activity:

$$\underset{2,5}{(CH_3)(C_2H_5)_2SiH} > \underset{1,2}{(CH_3)(C_2H_5)(Cl)SiH} > \underset{1}{(C_2H_5)(Cl)_2SiH} > \underset{0,9}{Cl_2SiH}$$

while with respect to ordinary addition they may be arranged in a somewhat different order:

$$(C_2H_5)(Cl)_2SiH > (CH_3)(C_2H_5)(Cl)SiH > Cl_2SiH > (CH_3)(C_6H_5)_2SiH.$$

The addition of even small amounts of $C_2H_5SiHCl_2$ to $CH_3(C_2H_5)SiH$ promoted addition of the latter to a substantial extent.

These facts can be explained on the basis of the assumption of the occurrence on the surface of the platinized charcoal of the following radical processes, starting with rupture of the Si—H bond in $C_2H_5(Cl_2)SiH$ which, obviously, is more readily adsorbed on the surface:

1. $C_2H_5SiHCl_2 \xrightarrow{Pt/C} C_2H_5\dot{S}iCl_2 + \dot{H}$;
2. $C_2H_5\dot{S}iCl_2 + HSi(CH_3)(C_6H_5)_2 \rightarrow C_2H_5SiHCl_2 + \dot{S}i(CH_3)(C_6H_5)_2$;
3. $(C_6H_5)_2(CH_3)\dot{S}i + CH_2=CH\cdot R \rightarrow (C_6H_5)_2(CH_3)SiCH_2\dot{C}HR$;
4. a) $(C_6H_5)_2(CH_3)SiCH_2\dot{C}HR + HSi(CH_3)(C_6H_5)_2 \rightarrow (C_6H_5)_2(CH_3)SiCH_2CH_2R +$
$+ \dot{S}i(CH_3)(C_6H_5)_2$ etc., or
b) $(C_6H_5)_2(CH_3)SiCH_2\dot{C}HR + \dot{H} \rightarrow (C_6H_5)_2(CH_3)SiCH_2CH_2R$.

TABLE 2

Deuterium Exchange Between $C_2H_5SiHCl_2$ and $CH_3(C_2H_5)_2SiD$ (the figures in parentheses refer to product in contact with the walls of the autoclave)

Expt. No	Type of experiment	Amt. of 1% Pt/C, g	T_{max}, °C	P_{max}, atm	Reaction time, hr	Amount in mixture, %			
						$C_2H_5SiHCl_2$	$CH_3(C_2H_5)_2SiH$	$(CH_3)(C_2H_5)_2SiD$	$C_2H_5SiDCl_2$
1	Heated in glass ampoule without catalyst	—	153	6	2	50 (30)	10 (22–25)	23 (a)	— (b)
2	Heated in autoclave with catalyst	0.2	168	9	2	(30)	(22–25)	(a)	(b)
3	Heated in glass ampoule with catalyst	0.05	168	7	2	30	22–25	a	b

Notes. a) The intensity of the Si–D Raman line for $(CH_3)(C_2H_5)_2SiD$ – 1527 cm^{-1} decreased considerably; b) a new intense line appeared at 1608 cm^{-1} in the Raman spectrum of this mixture; the frequency corresponds to the frequency of Si–D in the spectrum of $C_2H_5SiDCl_2$.

The initiation of the reaction can also be represented in a somewhat different form, namely as the addition of a $(C_2H_5)(Cl_2)Si$ radical to the unsaturated bond with the subsequent reaction of $(CH_3)(C_2H_5)_2SiH$, the Si–H bond of which ruptures under the influence of the $(C_2H_5)_2(CH_3)SiCH_2CHR$ radical more readily than does that of $C_2H_5(Cl_2)SiH$.

The first scheme indicates that deuterium exchange between $C_2H_5(Cl_2)SiH$ and $CH_3(C_2H_5)_2SiD$ would be possible under these reaction conditions in the presence of platinized charcoal.

The data of Table 2, which presents the data from deuterium exchange experiments, confirm this assumption. Deuteriumexchange did not occur in the absence of a catalyst. The catalyst and the walls of the reactor, on which there always remained platinum from the experiments with H_2PtCl_6, readily promoted deuterium exchange. With $C_2H_5SiHCl_2$, deuterium exchange occurred to the extent of approximately 50%. Considering the addition reaction as basically a homolytic reaction not only permits an explanation of a number of previously difficultly explainable facts, but also permits to some extent a better informed approach to the selection of catalysts for this commercially important reaction. Thus, it is well known that during the addition of silicon hydrides to acrylonitrile in the presence of free radical initiators, the latter readily polymerizes to give a mixture of high-boiling telomers. In the presence of platinized charcoal, where the process occurs on the surface of the catalyst, these reactions are suppressed to a significant extent, but they nevertheless occur. It might be assumed that these factors would not play the same role in a heterolytic mechanism. It is no accident that with acrylonitrile, bases are the most suitable catalysts for addition according to the scheme [10, 11]:

$$\equiv Si^{-}H^{+} + CH_2 = CH_2CN \rightarrow \equiv SiCH_2CH_2CN$$

In conformity with these considerations, we carried out the addition of trichlorosilane to acrylonitrile under the influence of dimethylcyanamide, and the reaction proceeded successfully. Dimethylcyanamide is a new catalyst for the addition of silicon hydrides to unsaturated compounds.

The addition undoubtedly proceeds in a more complex manner in the presence of H_2PtCl_6, which may be because the biggest part of the H_2PtCl_6 is reduced to Pt during the reaction. We suggest that in this case also, a homolytic mechanism better explains the experimental facts than does a heterolytic mechanism.

EXPERIMENTAL

1. Homolytic Hydrogenation of Diphenylpicrylhydrazyl (I) to Diphenylpicrylhydrazine (II).

The experiments were carried out under standard conditions at a temperature of 94°, both with and without a catalyst. The results of the experiments are presented in Table 1.

2. Methyldiethylsilicon deuteride $CH_3(C_2H_5)_2SiD$.

A mixture of 80 g (0.58 mole) of methyldiethylchlorosilane, 40 g (4.4 moles) of lithium deuteride, and 105 ml of absolute dibutyl ether was heated for 20 hours in a stainless steel autoclave fitted with a mechanical stirrer, a thermometer, and a fractionating column packed with nichrome packing. The reaction was carried out at the boiling point of the mixture, with vigorous stirring. The resulting crude product was redistilled, and 30 g (50%) of methyldiethylsilicon deuteride was obtained. According to the Raman data, this material contained about 24% $CH_3(C_2H_5)_2SiH$; b.p. 76.8° (735 mm) d_4^{22} 0.7102, n_D^{20} 1.3975.

3. Deuterium Exchange Between $C_2H_5SiHCl_2$ and $CH_3(C_2H_5)_2SiD$.

The effect of the catalyst (1% Pt/C) is shown by the data of Table 2. The experiments were carried out in glass ampoules, which were placed in an autoclave constructed of 1Kh18N9T stainless steel.* In order to determine the effect of the autoclave walls on deuterium exchange, an experiment was carried out in the autoclave itself. Reaction conditions for the deuterium exchange corresponded to those for the addition of these same hydrides and deuterides to unsaturated compounds in the presence of 1% Pt/C. Quantitative and qualitative analyses of the mixtures of reaction products were carried out by means of Raman and infrared spectroscopy.** The accuracy of the determinations was about 1-3%. The initially equimolar mixture contained 56% $C_2H_5SiHCl_2$ and 44% $CH_3(C_2H_5)_2$·SiD and $CH_3(C_2H_5)_2SiH$. According to the infrared data, these same mixtures contained 59% $C_2H_5SiHCl_2$, 31% $CH_3(C_2H_5)_2SiD$, and 10% $CH_3(C_2H_5)_2SiH$. From 11 to 46 g of the equimolar mixture was used for the reaction, along with an appropriate amount of catalyst (0.1 g of 1% Pt/C for each 0.2 mole of the mixture). A comparison of experiments 1 and 3 clearly indicates that under the conditions used for the addition reactions, 1% Pt/C catalyzes deuterium exchange between $C_2H_5SiHCl_2$ and $CH_3(C_2H_5)SiD$. Moreover, approximately 50% of the $C_2H_5SiHCl_2$ reacted. As experiment 1 shows, the effect of the autoclave walls, on which traces of platinum were deposited, during experiments with H_2PtCl_6, was the same as the effect of the 1% platinized charcoal.

4. β-Trichlorosilylpropionitrile — $Cl_3SiCH_2CH_2CN$.

A mixture of 40.6 g (0.3 mole) of trichlorosilane, 15.5 g (0.3 mole) of acrylonitrile, and 3 g (0.043 mole) of dimethylcyanamide was charged to a glass vessel, which was then placed in a test autoclave and gradually heated for 2 hours. When the temperature reached 124°, it jumped to 168° and the pressure increased to 8 atm at the same time. The crude reaction products were twice distilled under vacuum, and 20.3 g (37%) of pure β-trichlorosilylpropionitrile was obtained: b.p. 92-94° (15 mm), m.p. 34-35°. The literature gives 32-33° for the melting point [12].

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* This steel contains (in percent): C ~ 0.08, Mn ~ 1.22, Si ~ 0.34, P ~ 0.026, S ~ 0.01, Cr ~ 17.45, Ni ~ 10.48, Ti ~ 0.42.

** We are indebted to Yu. P. Egorov for carrying out the analyses.

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CALORIMETRIC DETERMINATION OF THE HEATS OF FORMATION OF FERRITES

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The literature contains comparatively few reports of work devoted to the determination of the thermodynamic functions of ferrites. For practical reasons, the synthesis of ferrites requires the determination of the free energies and heats of formation of ferrites. We have determined the heats of formation of copper, zinc, and calcium ferrites from the differences in the heats of interaction of mixtures of the oxides and ferrites at 413°K with a mixture of sulfuric and phosphoric acids; the method has previously been described in connection with the determination of the heat of formation of magnesium ferrite.

	Starting material					
	$CuO + Fe_2O_3$, $8.003 \cdot 10^{-4}$ mole	$CuFe_2O_4$, $8.003 \cdot 10^{-4}$ mole	$ZnO + Fe_2O_3$, $8.1 \cdot 10^{-4}$ mole	$ZnFe_2O_4$, $8.1 \cdot 10^{-4}$ mole	$CuO + Fe_2O_3$, $8.63 \cdot 10^{-4}$ mole	$CaFe_2O_4$, $8.63 \cdot 10^{-4}$ mole
Heat of solution $-\Delta H$, kcal/mole	61,5±0,9	59,9±0,4	62,8±0,3	55,8±0,5	87,7±0,8	68,6±0,9
Heat of formation of the ferrite from the oxides $-\Delta H$, kcal/mole	1,6		7,0		19,1	

The copper and zinc ferrites were prepared by thermal decomposition of the isomorphic schoenites having the composition $\frac{1}{3}MSO_4 \cdot \frac{2}{3}FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ where M is Cu or Zn. The calcium ferrite was prepared via the ceramic route with calcination at 1100°. Throughout the entire series of experiments, equal weights of ferrites and the corresponding mixtures of ferrite-forming oxides were used in order that the final solutions would be at the same dilution. The results of the experiments on the determination of the heats of solution of the mixtures of oxides and ferrites in the acid at 413° K are presented in the table.

Taking into account the heat of formation of $MgFe_2O_4$ from MgO and Fe_2O_3, $-\Delta H_{413} = 9.2$ kcal/mole-it is evident that there is a decrease in the exothermic heat of formation of ferrites from the oxides in the series Ca, Mg, Zn, Cu, which is in agreement with the electromotive series of metals. The very low exothermic effect during the formation of $CuFe_2O_4$ from the oxides is in good agreement with the thermal instability of $CuFe_2O_4$ above 1100°, where there is thermal dissociation according to $4CuFe_2O_4 = 2Cu_2O + 4Fe_2O_3 + O_2$.

For the calculation of the heats of formation of $CuFe_2O_4$ and $ZnFe_2O_4$ from the elements at 413°K, use was made of the C_p equation and the values of ΔH_{298} for the oxides [1, 2]. From these data, and using the heats of formation from the oxides determined in the present work, we calculated a value of −233.7 kcal/mole for ΔH_{413} for $CuFe_2O_4$ and a value of −284.9 kcal/mole for H_{413} for $ZnFe_2O_4$. It is possible to recalculate the thermodynamic data for magnesium and calcium ferrites to 298°K, since their heat capacities have been determined by King and Bonnickson [3, 4]. The heats and free energies of formation of magnesium and calcium ferrites are presented below.

	$-\Delta H_{298}$ kcal/mole	$-\Delta F_{298}$ kcal/mole
$MgFe_2O_4$	349.9	322.9
$CaFe_2O_4$	365.9	340.2

Two determinations of the heat of formation of calcium ferrite are described in the literature. Marchal [5] obtained for the heat of formation of $CaFe_2O_4$ $\Delta H = -398$ kcal/mole. Later, Honus found $\Delta H_{298} = -364.5$ kcal/mole. The value obtained by Honus is in agreement with our determination ($\Delta H_{298} = -365.9$ kcal/mole).

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SYNTHESIS OF POTASSIUM DISULFOTRICYANOAQUOCOBALTATE

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Mixed cyano complexes of metals of the prusside type have been investigated to a considerably lesser extent than have the corresponding homogeneous compounds. This is even more the case with respect to sulfur-containing cyano complexes of metals, of which only the few representatives described in papers by E. Pechard [1], V. Heide and K. Hofman [2], and E. Crepaz [3] are known. More recent literature [4] mentions sulfur-containing complex iron cyanides of the composition $Na_{6n}[Fe_2(CN)_5S_2]_n$, the formation of which permits detection of sulfur ions in an alkaline medium.

Our previous work [5-7], which was devoted to hydroxosulfotetracyanomolybdates, showed that it is possible to replace to hydroxyl group by a sulfur ion.

It seems desirable to attempt this reaction with other metals which form hydroxocyano compounds. One such possible metal is cobalt, which forms the compound $K_3[Co(OH)(CN)_5]\cdot H_2O$; this compound has been prepared by L. Smith, J. Kleinberg and E. Griswold [8]. The starting trivalent cobalt compound was prepared by the method of the above authors by the action of the calculated amount of potassium cyanide on cobalt nitrate and further oxidation of the potassium pentacyanoaquocobaltate with atmospheric oxygen.

We studied the interaction of this compound with potassium sulfide, which proceeds according to

$$K_3[Co^{3+}(OH)(CN)_5] + 2K_2S + H_2O = K_4[Co^{3+}(CN)_3S_2(H_2O)] + 2KCN + KOH.$$

Potassium sulfide was added to 30% solutions of the original cobalt compound in molar ratios of 1:1 and 1:2.

In both cases there was observed a gradual change in the color of the solution from dark brown to a yellowish orange. The reaction took place at room temperature over a period of several hours, and the product was separated on the following day by means of ethyl alcohol. The compound formed coarse rhombic crystals having a dark amber color. The product had the same composition regardless of the amount of potassium sulfide introduced.

Chemical analysis gave the following results:

Found %: K 35.21; 34.82; Co 12.82; 12.63; N 9.03; 9.11; S 13.91; 13.74; H_2O 19.93; 19.87 $K_4[Co(CN)_3S_2(H_2O)]\cdot 4H_2O$. Calculated %: K 34.94; Co 13.17; N 9.38; S 14.33; H_2O 20.18

Measurements of the electrical conductivity of a solution of the compound was carried out to determine the coordination formula. The molar conductivity at a dilution of 1 mole per 1000 liters was $\mu^{25}_{1000} = 580.5$ ohm^{-1} cm^2, which corresponds to an electrolyte yielding five ions. The composition of this compound can be expressed by the formula $K_4[Co(CN)_3S_2(H_2O)]\cdot 4H_2O$.

Four of the water molecules, which can be removed at a temperature of 110°, constitute water of crystallization. One molecule of H_2O is bound more tightly, and we consider it to be coordination bonded and place it in the inner sphere of the complex.

When a solution of the complex salt is treated with a solid base, a complex compound containing less sulfur precipitates.

Nitric acid, 10% hydrogen peroxide, and other oxidizing agents decompose the complex with simultaneous oxidation of the sulfur.

Cations of heavy and cyanophilic metals react with this sulfur-containing complex cyanide of trivalent cobalt to form colored precipitates of difficultly soluble compounds. Mn^{2+}, Zn^{2+}, and Cd^{2+} give white precipitates; Fe^{2+}, Cu^{2+} and Ni^{2+} give light-green precipitates; Co^{2+} gives a light-orange precipitate; Ag^{+} gives a beige precipitate; and Fe^{3+} gives a green precipitate. Hg^{2+} and Pb^{2+} form yellow precipitates, which indicates the absence of free sulfur ions and confirms the high stability of the complex. The reaction by which the potassium disulfotricyanoaquocobaltate was prepared confirms that it is possible to replace water molecules and hydroxyl and cyano groups by sulfur ions not only in the case of molybdenum, but also in the case of cobalt.

It may be assumed that such a reaction is also possible in the case of other cyano complexes of metals.

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ALKYLATION OF 4-FLUOROPHENOL WITH PROPYLENE AND CYCLOHEXENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$ AND $BF_3 \cdot O(C_2H_5)_2$

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The literature contains no reference at all on the reaction of fluorophenols with olefins. During the course of investigations in the general field of alkylation of halophenols with olefins in the presence of catalysts based on boron trifluoride [1-6], we studied the reaction of 4-fluorophenol with propylene and cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$, and the present communication reports the results of this study.

In contrast to the previously studied chloro- and bromophenols, 4-fluorophenol is highly reactive, and, when reacted with olefins, particularly propylene, it forms a rather complex mixture of products. In this case, along with isopropyl 4-fluorophenyl ether, isopropyl isopropylfluorophenyl ether is always formed, and isopropylfluorophenol is also formed under certain conditions. The yield of products depends on the nature and amount of the catalyst, the temperature, and the mole ratio of the reactants. Thus, at 60° in the presence of $BF_3 \cdot O(C_2H_5)_2$, the milder catalyst, only the ether products are obtained, and phenol products are absent, at least in perceptible amounts. In the presence of $BF_3 \cdot H_3PO_4$, the yield of phenol compounds is higher the higher the temperature within the range of from 40-70°.

The best conditions, under which isopropyl 4-fluorophenyl ether is obtained in 54% yield, are a mole ratio of fluorophenol to propylene to $BF_3 \cdot H_3PO_4$ of 3:1:0.4 and a temperature of 40°; for the preparation of isopropyl 4-fluorophenyl ether in 36% yield, the conditions are a mole ratio of reactants and catalyst of 5:1:0.3 and a temperature of 60°; while for the preparation of isopropyl-4-fluorophenol with a maximum yield of 38%, the ratio of reactants and catalyst is 3:1:0.2 and the temperature is 70°.

The effect of temperature, amount of catalyst, and mole ratio of reactants on the over-all yield of the products indicated above is apparent from the experimental data presented in Table 1.

The 4-fluorophenol reacts with cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ to yield a single product — cyclohexyl 4-fluorophenyl ether — with a maximum yield of 70.7% of theoretical. Even after the initial distillation of the alkylate, the product boiled within a range of 2-3°, as may be seen from the data of Table 2. The ether compounds were identified by cleavage to the corresponding phenols and conversion of the latter to the phenoxyacetic acids.

EXPERIMENTAL

The 4-fluorophenol was prepared by demethylation of 4-fluoroanisole [7]; m.p. 46°. The propylene, cyclohexene, and catalysts were prepared as described previously [5].

TABLE 1

Alkylation of 4-Fluorophenol with Propylene in the Presence of $BF_3 \cdot H_3PO_4$ and $BF_3 \cdot O(C_2H_5)_2$

Exp. No.	Mole ratio of fluorophenol to propylene to catalyst, $BF_3 \cdot H_3PO_4$	Reaction temp. °C	Propylene addition time, hr	Alkylation products								
				isopropyl-4-fluorophenyl ether			isopropyl 2-isopropyl-4-fluorophenyl ether			2-isopropyl-4-fluorophenol		
				% of theor.	boiling range, °C/mm	n_D^{20}	% of theor.	boiling range, °C/mm	n_D^{20}	% of theor.	boiling range, °C/mm	n_D^{20}
1	2:1:0,2	60	2	8,3	37—50/3	1,4755	28,5	71—80/4	1,4912			
2	2:1:0,4	60	2,5	0,5	42—44/2	1,4753	25,8	88—96/8	1,4923			
3	2:1:0,4	40	2	28,3	56—60/6	1,4748	29,6	82—90/7	1,4910	16,4	80—85/5	1,5040
4	3:1:0,1	40	7	42,4	52—60/5	1,4750	10,4	77—82/6	1,4930	12,0	80—85/5	1,5042
5	3:1:0,2	40	2,5	41,1	53—60/6	1,4760	28,8	76—82/6	1,4937			
6	3:1:0,2	50	2	38,8	44—47/4	1,4750	25,8	73—80/4	1,4922			
7	3:1:0,2	60	4	52,3	46—52/4	1,4758	33,2	74—80/4	1,4912	5,8	81—86/5	1,5022
8	3:1:0,2	70	2	4,6	56—60/6	1,4748	32,9	82—90/7	1,4928	38,1	78—81/4	1,5045
9	3:1:0,3	40	2	50,6	40—46/2	1,4750	29,9	71—80/3	1,4913			
10	3:1:0,4	40	1,5	54,0	44—50/3	1,4754	23,1	72—80/3	1,4920			
11	4:1:0,4	40	3	45,5	56—60/6	1,4750	31,0	82—90/7	1,4910	5,3	80—87/6	1,5028
12	5:1:0,3	60	2	30,8	52—60/5	1,4753	36,3	79—85/6	1,4920	10,4	82—88/6	1,5020
13	5:1:0,4	60	2	19,1	52—60/5	1,4756	28,0	80—84/6	1,4917	32,4	81—87/6	1,5040

Note. In each experiment, 0.1-0.2 mole of propylene and the calculated amounts of 4-fluorophenol and catalyst were used. Experiments 1 and 2 were carried out in the presence of boron trifluoride etherate. The temperature varied ± 2° from that indicated in the table.

TABLE 2

Alkylation of 4-Fluorophenol with Cyclohexene in the Presence of $BF_3 \cdot H_3PO_4$

Expt. No.	Mole ratio of fluorophenol to cyclohexene to $BF_3 \cdot H_3PO_4$	Reaction temp. °C	Reaction time, min	Cyclohexyl 4-fluorophenyl ether		
				% of theor.	Boiling range °C/mm	n_D^{20}
1	2:1:0,2	40	40	63,5	88—90/2	1,5065
2	3:1:0,1	40	40	63,7	90—94/3	1,5065
3	3:1:0,2	40	50	70,7	84—86/1	1,5068
4	3:1:0,2	60	60	64,2	88—92/2	1,5066
5	3:1:0,3	40	60	59,3	82—85/1	1,5066

TABLE 3

Compound	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D	
				found	calc.
Isopropyl 4-fluorophenyl ether	49/4	1,0340	1,4745	41,90	41,59
Isopropyl 2-isopropyl-4-phenyl ester	77,5—78/5	1,0284	1,4906	55,18	55,44
2-Isopropyl-4-fluorophenol	81—82/6	1,0942	1,5047	41,69	41,48
2-Isopropyl-4-fluorophenoxyacetic acid.	M.p. 124°				
Cyclohexyl 4-fluorophenyl ether	95—96/3	1,0767	1,5070	53,70	53,38

Alkylation of 4-Fluorophenol with Propylene. The reaction was carried out in the usual manner [6] in a three-neck flask. In the experiments with boron trifluoride etherate, the fluorophenol and catalyst were charged to the flask, the mixture was heated to 60°, and with vigorous stirring, the propylene was introduced at a rate of 1.2-2 liters/hour. As the propylene was introduced, the reaction mixture acquired a brown color, which toward the end became dark brown. After the calculated amount of propylene had been added, the mixture was stirred for an additional two hours at the temperature of the experiment and then was allowed to stand for 12 hours at room temperature. The mixture, which was a rather viscous oil, was then mixed with benzene and treated repeatedly with small portions of a 10% aqueous solution of NaOH until the phenol products had been completely extracted (by test with a drop of hydrochloric acid). The ether products, which were a transparent, almost colorless oil, were washed well with water, dried with calcium chloride, and distilled into fractions having boiling ranges of from 2-10°. The phenol products, which were dissolved in the alkaline solution, were treated with concentrated HCl, extracted with ether, dried with sodium sulfate, and distilled into fractions with boiling ranges of 3-6°. For purposes of identification, the fractions were redistilled into narrower fractions. The isopropyl 2-isopropyl-4-fluorophenyl ether was converted by heating with HBr to 2-isopropyl-4-fluorophenol, and 2-isopropyl-4-fluorophenoxyacetic acid was obtained from the latter by reaction with chloroacetic acid.

Alkylation of 4-Fluorophenol with Cyclohexene. The reaction was carried out in a three-neck flask, with vigorous stirring. To a mixture of 4-fluorophenol and $BF_3 \cdot H_3PO_4$, preheated to the predetermined temperature, there was slowly added from a dropping funnel 0.1 mole of cyclohexene. The reaction mixture, a brown liquid, was treated as in the case of propylene alkylation. In this case, the only reaction product was cyclohexyl 4-fluorophenyl ether, which, even after the initial distillation of the alkylate, was obtained in a fairly pure form. A second distillation yielded a colorless oil with an agreeable ethereal odor. The physicochemical constants of the products are presented in Table 3.

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THE SIGMA PHASE IN THE SYSTEM RHENIUM – VANADIUM

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(Presented by Academician I. P. Bardin, December 2, 1959)

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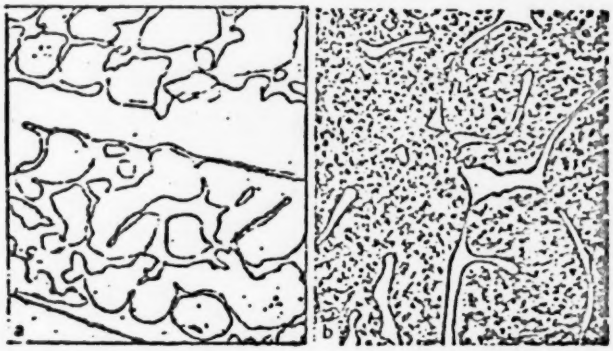
A sigma phase, as is well known, is a metallic compound with the structure of β-U and has a tetragonal lattice with 30 atoms in the unit cell. A sigma phase is encountered in alloys of the metals of subgroups V A and VI A of the periodic system of D. I. Mendeleev with the transition metals of groups VII A and VIII. A high hardness – of the order of 1200-1500 kg/mm^2 Vickers – is characteristic of the sigma phase.



Microstructure of the alloy containing 90 wt % (71.4 atom %) rhenium, 500 x. a) Cast: ($\alpha + \sigma$); b) annealed at 1500° for 5 hours, $\alpha + (\alpha + \beta)$.

According to the literature and to our experimental data, rhenium (which is a metal of subgroup VII A) forms a sigma phase with the transition metals of subgroup IV A (zirconium), subgroup V A (niobium and tantalum), subgroup VI A (chromium, molybdenum, and tungsten), subgroup VII A (manganese) and group VIII (iron), and the dimensional factor varies from + 16.6% (Zr) to – 8% (Fe). An electron concentration of the order of 6.6 to 7.6 electrons/atom is characteristic of the sigma phase in systems containing rhenium [1-9]. On the basis of these data, particularly the data regarding Nb and Ta, it may be assumed that rhenium should also form a sigma phase with the elements of subgroup V A (vanadium); however, in our previous work on the system rhenium – vanadium [1], no intermediate phases were found.

As a result of our work investigating the equilibrium diagram of the system vanadium – rhenium [10], it has been established that a sigma phase exists in the system over a narrow interval of homogeneity at a rhenium content of about 75 atom % (VRe_3). This phase is formed by a peritectic reaction at 2490° between the melt and a

hkl	Intensity	Zr — Re		V — Re		Nb — Re		Ta — Re	
		sin θ	d×0.872 Å	sin θ	d×1.016 Å	sin θ	d×1.003 Å	sin θ	d×0.996 Å
112	s.	0,4480	2,340	0,5030	2,309	0,541	2,294	0,4884	2,305
410									
330	av.	0,4658	2,257	0,5180	2,243	0,551	2,247	0,5046	2,260
202	v.w.	0,4775	2,204	0,5299	2,193	0,563	2,202	0,5108	2,195
212	w.	0,4909	2,163	0,5439	2,137	—	—	0,5294	2,132
420									
411	s.	0,5109	2,062	0,5548	2,093	0,590	2,098	0,5377	2,101
331	av.	0,5215	2,021	0,5678	2,048	—	—	0,5655	2,042
	a, Å	10,12		9,36		8,75		9,67	
	c, Å	5,42		4,86		4,06		4,97	
	c/a	0,535		0,52		0,52		0,52	

hkl	Intensity	Cr — Re		Mo — Re		W — Re		Mn — Re		Fe — Re	
		sin θ	d×1.037 Å	sin θ	d	sin θ	d×1.003 Å	sin θ	d×1.044 Å	sin θ	d×1.038 Å
112	s.	0,5120	2,316	0,4957	2,308	0,497	2,308	0,5169	2,309	0,5234	2,311
410											
330	av.	0,5275	2,247	0,5089	2,247	0,512	2,250	0,5312	2,248	0,5390	2,245
202	v.w.	0,5385	2,202	0,5194	2,202	0,524	2,189	0,5416	2,205	0,5505	2,197
212	w.	0,5530	2,143	0,5338	2,142	0,535	2,143	0,5569	2,143	0,5644	2,144
420											
411	s.	0,5675	2,090	0,5454	2,097	0,547	2,097	0,5707	2,092	0,5757	2,101
331	av.	0,5800	2,044	0,5594	2,044	0,560	2,048	0,5858	2,039	0,5919	2,045
	a, Å	9,33		9,54		9,54		9,14		9,02	
	c, Å	4,80		4,96		4,97		4,75		4,69	
	c/a	0,52		0,52		0,52		0,52		0,52	

solid solution of vanadium in rhenium. The microhardness of the sigma phase is about 2000 kg/mm^2 as measured with a PMT-3 apparatus at a load of 100 g.

In order to establish the temperature interval over which the sigma phase exists, a series of high-temperature annealings of cast alloys was carried out (1750° for 7 hours; 1500° for 5 hours; 1000° for 450 hours). The x-ray investigation was carried out using an RKD-type camera and CrK_α radiation. The data from the x-ray and microstructural investigations established the presence of a eutectoid decomposition of the sigma phase at 1500° with the formation of a mixture of two solid solution: a vanadium-rich (α) and a rhenium-rich (β) solution (Fig. 1, a and b).

The x-ray pattern of the cast alloy showed a system of lines characteristic of a sigma phase (see table); calculation of the lattice parameters gave a = 9.36 A, c = 4.86, A, and c/a = 0.52.

The table presents comparative data calculated from x-ray patterns of sigma phases in systems formed by rhenium with zirconium [4], vanadium and niobium [5], tantalum and chromium [6], molybdenum [7, 8], tungsten [9], and manganese and iron [8]; the patterns were obtained with CrK_α radiation.

In comparing these data, one's attention is attracted by a certain difference in the phase in the Zr—Re system, which we assigned to the type of phase related to sigma phases: This phase differs from the remaining sigma phases. It is probable that this difference is due to the fact that the formation of a sigma phase is not a characteristic of the metals of subgroup IV A, and the appearance of a sigma phase in the rhenium—zirconium system can be considered an exception.

Moreover, it is interesting that a sigma phase is formed in the rhenium—manganese—iron system, the latter two elements belonging to groups VII A and VIII [8]. This indicates an anomalous behavior of rhenium as compared to the metals of other groups.

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SYNTHESIS OF 6-ALKYLTETRALINS

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In connection with our investigation of the alkylation of tetralin, it became necessary to synthesize certain 6-alkyltetralins for use as standards in the analysis of catalyzates by infrared spectroscopy.

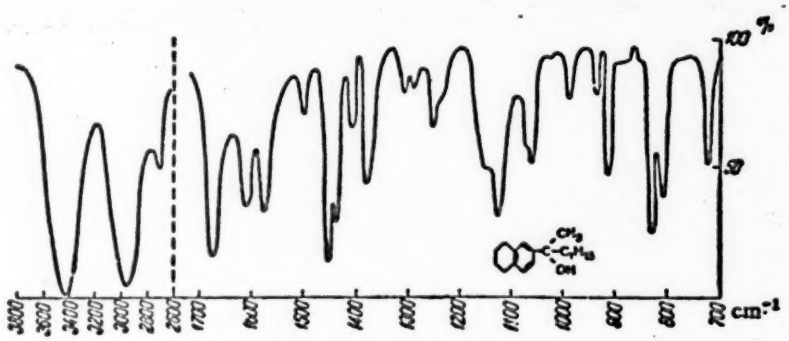

Fig. 1

Preparation of 6-alkyltetralins in the pure form by interaction of tetralin with alkyl bromides in the presence of $AlCl_3$ appeared to be practically impossible, since in this reaction, along with the β-isomer, there is obtained up to 30% yield of the α-isomer [1], which is extremely difficult to separate. It is known from the work of Schroeter [2] and Levy [3] that hydrogenation of 2-alkylnaphthalenes in the presence of a nickel catalyst yields chiefly 6-alkyltetralins. However, the more recent work of Bailey and co-workers [4] has shown that hydrogenation of 2-alkylnaphthalenes yields a mixture of 2-alkyl- and 6-alkyltetralins in a ratio of 1:2.

Therefore, it was decided to carry out the synthesis of 6-alkyltetralins according to the following schemes:

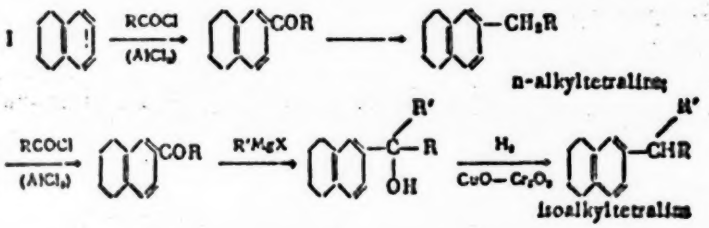

TABLE 1

Properties of 1,2,3,4-Tetrahydro-6-naphthyl Alkyl Ketones

Ketone	B.p., °C/mm	d_4^{20}	n_D^{20}	C, % found	C, % calc.	H, % found	H, % calc.	Yield, %
	201/15	1,0090	1,5406	83,28	83,01 82,89	9,32	9,24 9,28	60,6
	167—168/2	0,9986	1,5358	83,42	83,28 83,20	9,61	9,77 9,91	66,0
	183—185/4	0,9844	1,5319	83,55	83,15 83,20	9,90	9,82 9,97	61,6
	191—192/4	0,9789	1,5282	83,66	83,63 83,61	10,14	10,18 10,36	81,6
	199—200,5/3	0,9655	1,5218	83,86	83,45 83,40	10,56	10,70 10,43	60,7

TABLE 2

Properties of the 6-Alkyltetralins

Alkyltetralin	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D calc.	MR_D found	C, % calc.	C, % found	H, % calc.	H, % found
	124—125,5/3	1,5184	0,9236	65,67	66,42	89,02	88,63 88,70	10,98	10,87 10,97
	162—163/4	1,5128	0,9142	74,91	75,74	88,62	87,97 87,91	11,38	11,75 11,89
	185,5—186,5/4	1,5060	0,9045	88,76	89,21	88,15	88,36 88,20	11,85	11,47 11,40
	157/4	1,5079	0,9077	84,14	84,80	88,29	88,30	11,71	11,71
	145—145,5/4	1,5110	0,9112	84,14	84,87	88,29	88,40	11,71	11,51

Alkylation of tetralin was carried out by the method of Friedel and Crafts in nitrobenzene medium, since there are indications in the literature that alkylation of tetralin in carbon disulfide medium yields 2% of the α-isomer [1], while in nitrobenzene, substitution occurs only in the β-position [5].

By the interaction of tetralin with the chlorides of the appropriate acids in nitrobenzene medium at 0° in the presence of $AlCl_3$, we were able to obtain 1,2,3,4-tetrahydro-6-naphthyl- butyl, n-amyl, n-heptyl, and n-nonyl ketones, the properties of which are presented in Table 1.

The tertiary alcohols were synthesized via the Grignard route. 8-(1,2,3,4,-Tetrahydro-6-naphthyl)-8-nonanol, b.p. 180.5-182.5° (3 mm), $n^{20}D$ 1.5219 and d^{20}_4 0.9728 was obtained by reaction of CH_3MgI with 1,2,3,4-tetrahydro-6-naphthyl heptyl ketone.

Found %: C 82.84; 82.88; H 10.71; 10.71 $C_{19}H_{30}O$. Calculated %: C 83.14; H 11.03

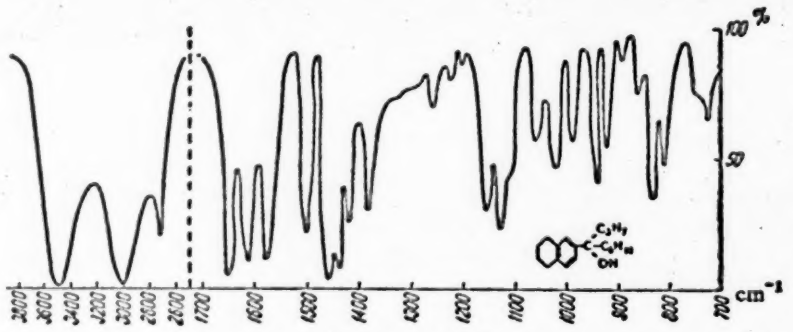

Fig. 2

·6-(1,2,3,4-Tetrahydro-6-naphthyl)-6-nonanol, b.p. 162-163° [1], $n^{22}D$ 1.5268 and d^{22}_4 0.9764, was obtained by the action of n-C_3H_7MgBr on 1,2,3,4-tetrahydro-6-naphthyl amyl ketone.

Found %: C 83.25; 83.05; H 10.50; 10.30 $C_{19}H_{30}O$. Calculated %: 83.14; H 11.02

The infrared spectra of these alcohols are shown in Figs. 1 and 2.*

The tertiary alcohols were reduced in an autoclave in the presence of copper chromite [6] at 120 atm and 240°. Since partial dehydration of the alcohols could have occurred under these conditions, the hydrogenation products were subjected to an additional hydrogenation in the presence of Raney nickel at 50° and 70 atm hydrogen pressure. The properties of the resulting 6-(1-methyloctyl)tetralin and 6-(1-n-propylhexyl)tetralin are presented in Table 2.

The 6-n-amyltetralin, 6-n-heptyltetralin, and 6-n-decyltetralin were prepared by reduction of the corresponding ketones by a modification of the Wolff-Kishner method [7]: decomposition of the hydrazones with sodium in diethylene glycol medium.

The properties of all hydrocarbons synthesized are shown in Table 2. This is the first preparation of 6-(1-methyloctyl)tetralin, 6-(1-n-propylhexyl)tetralin, 8-(1,2,3,4-tetrahydro-6-naphthyl)-8-n-nonanol, and 6-(1,2,3,4-tetrahydro-6-naphthyl)-6-n-nonanol. The constants of the normal alkyltetralins are in good agreement with the values reported in the literature [8, 9].

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* The infrared spectra were obtained by E. D. Lubuzh, to whom the authors express their appreciation.

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AN INVESTIGATION OF THE STRUCTURE OF THE BORIC OXIDE MOLECULE, B_2O_3, BY ELECTRONIC DIFFRACTION

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The problem of the structure of oxygen compounds of boron has recently attracted the attention of investigators. A large amount of work has been devoted to the study of the structure of boron oxide in the glass and crystalline states (see, for example, monograph [1]). However, up to the present time, there have been published no experimental data on the configuration and geometric parameters of B_2O_3 molecules in the gas phase. Acquisition of such data is of great interest for the establishment of regularities in the structures of molecules of the type X_2Y_3 and is also required for calculation of the thermodynamic functions and the equilibrium constants of certain gas-phase reactions by statistical thermodynamics.

The purpose of the present investigation was the determination, by electron diffraction methods, of the geometric structure of the B_2O_3 molecule in the vapor phase. The work was carried out using the electron diffraction apparatus at the Moscow State University. This apparatus, which is used for the investigation of molecules of difficultly vaporized compounds, includes a high-temperature vaporizer (which heats the tubes containing the samples by electron bombardment) and a rotating sector [2]. The preparation of boric oxide used in the present investigation was obtained by prolonged dehydration of boric acid ("CP" grade). Prior to taking an electron diffraction pattern, the boric oxide was charged to a tube which was then placed in the vaporizer, and the boric oxide was refused and degassed for a prolonged period under high vacuum (directly in the diffraction apparatus). Vaporization of the boric oxide was carried out at temperatures of the order of 1500-1800°, using molybdenum tubes and tungsten tubes with molybdenum caps; the two types of tubes gave the same results.* The patterns were taken on diapositive plates covered with black India ink (for protection from radiation from the vaporizer) using one- and two-lobe s^2- and s^3-sectors; different electron-accelerating voltages were used (λ = 0.0428-0.562 A), and the exposures were varied from a few seconds to 1-2 minutes.

Seven series of diffraction patterns (three exposures in each series) suitable for photometric measurements were obtained from the B_2O_3 vapors; of these, certain series were measured visually, while the remainder were measured photometrically. Interpretation of the electron diffraction patterns was carried out by two methods — by the radial distribution method of J. Karle and I. Karle [3-5] and by successive approximations [6] using the photometric data. The methods of treatment and interpretation of electron diffraction patterns have been described in detail in previous communications from our laboratory [2, 7]. It may be remarked that during the course of the investigation, numerous experimental difficulties had to be overcome, and the work was carried out over the course of several years.

* Tantalum tubes could not be used owing to the very considerable corrosion occurring under the conditions of our experiments.

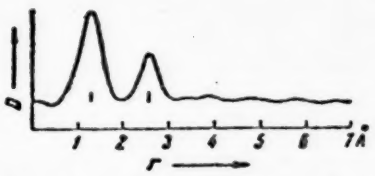
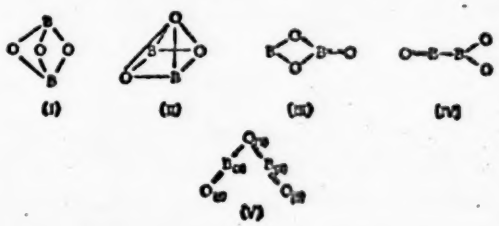


Fig. 1. Radial distribution [D(r)] curve for the boric oxide molecule.

The radial distribution curve[the D(r) curve] constructed from the experimental data is shown in Fig. 1. The initial portion of the intensity curve ($s = 0-4\ A^{-1}$), which was not available by experimental determination, was extrapolated from the theoretical I (s) curve for the group of atoms O−B=O with the values: r(B−−O)=1.36 A, r(B=O) 1.20 A, and r(O . . . O) 2.56 A, since these atoms make the major contribution to the molar dispersion of B_2O_3 (see below). As may be seen from Fig. 1, the D(r) curve has only two sharply expressed peaks; these occur at 1.28 and 2.56 A.

Interpretation of the electron diffraction patterns and of the D(r) curve is impossible without information on the composition of boric oxide vapor, since B_2O_3, B_4O_6, and BO_2 molecules can give a similar scattering picture (see the more detailed discussion in reference [8]). Reference [9] refers to an unpublished mass spectroscopic investigation by Bredt, who found that the chief component of boric oxide vapor at 1300° is the monomer B_2O_3. In order to confirm these data, we carried out a mass spectroscopic study of the composition of the vaporization products of boric oxide [10]; the results confirmed the data of Bredt and proved to be close to the measurements of Ingram, Porter, and Chupka, published shortly thereafter [11]. On the basis of the mass spectroscopic investigations of the composition of the vapor [10, 11] and on the basis of the determination of the molecular weight of the vapor [12], which indicated the presence of the B_2O_3 molecule in boric oxide vapors, it was possible to interrupt our electron diffraction data. We note that the electron diffraction patterns of boric oxide and boron sulfide [13] show that there is a great similarity in the intensity distribution of the scattered electrons in the two cases; this suggests that the structures of the molecules of these two compounds are quite similar.

We tested the following molecular models for B_2O_3:



From a consideration of the D(r) curve, one can conclude that the bipyramid model (I) of B_2O_3 is unsuitable. As in the case of boron sulfide [13], the D(r) curve has two sharply defined peaks, and the value of r_2, 2.56 A, for the second peak is twice the value of r_1, 1.28 A, for the first peak; it is evident that a bipyramid cannot be constructed with these parameters. Similar considerations force rejection of models (II)-(IV). These conclusions are confirmed by the successive approximation calculations. In Fig. 2 are presented the theoretical curve for the bipyramid structure of B_2O_3 with r(B−O) = 1.36 A, ∠ OBO = 84° and ∠ BOB = 78°, and also the theoretical curves 2-4 corresponding to models (II)-(IV), which, within the region of diffraction angles under consideration, have no similarity to the experimental curve.

Let us consider the question of the correspondence of the D(r) curves and model (V). The first peak at 1.28 A can be interpreted as a composite of two close-lying peaks which correspond to the interatomic distances $B_{(3)}-O_{(1)}$ and $B_{(3)}=O_{(4)}$,* and which are not resolved on the D(r) curve; the second peak at 2.56 A relates the interatomic distance $O_{(1)} . . . O_{(4)}$. Since the interatomic distance r_2 is twice as great as r_1, it inevitably follows that the atomic group O−B=O is linear. The ratio of the areas of the two peaks on the i) curve, 2.7, is close to the theoretical value for model (V), 2.5, while it differs sharply for the remaining models.

In interpreting the radial distribution curve there arises the question of why the D(r) curve has no peaks corresponding to greater interatomic distances. From an analysis of the theoretical I(s) curve for model (V) it was found that the basic motif of the electron diffraction patterns − alternation of four intense maximums and a stepwise intensity (low-intensity maximums) on the outside of these maximums (see the experimental curve of Fig. 2)−

* In this B_2O_3 model the number of interatomic bonds of each of these types is the same; therefore, the value r_1 is equal to half the sum of the distances $B_{(3)}-O_{(1)}$ and $B_{(3)}=O_{(4)}$.

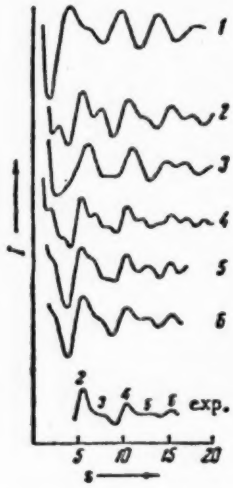


Fig. 2. Theoretical intensity curve for the different models of boric oxide and the experimental curve.

is determined by the sum of three harmonics corresponding to the interatomic distances $B_{(2)} - O_{(1)}$, $B_{(2)} = O_{(4)}$ and $O_{(1)} \ldots O_{(4)}$. Consequently, the amplitudes of the three fundamental harmonics, which correspond to the interatomic distances $B_{(1)} \ldots B_{(3)}$, $B_{(2)} \ldots O_{(5)}$ and $O_{(4)} \ldots O_{(5)}$, are small as compared to the amplitudes of the three first harmonics. This indicates that the amplitudes of the thermal vibrations of these pairs of atoms which are not bonded to each other are quite small. This is a natural conclusion, since a B_2O_3 model of the type of (V) would lead one to expect large deformation vibrations of the valence angle of the central oxygen atom at the high temperatures of our experiments, which should lead to a smoothing out of the peaks on the D(r) curve in the region of r > 3 A. It is interesting to note that the D(r) curve of boron sulfide [13] has peaks corresponding to unbonded pairs of atoms; this can be explained by the high nuclear charge of the sulfur atom and to the lower temperatures used in investigating the B_2S_3 molecule, owing to which the conditions for diffraction by unbonded pairs of atoms are more favorable than in the case of the B_2O_3 molecule.

Let us turn now to the successive approximation method. Theoretical curve 5 for model (V), which has the parameters $r(B_{(2)} - O_{(1)}) = 1.36$ A, $r(B_{(2)} = O_{(4)}) = 1.20$ A and $\angle$ BOB = 95°, agrees satisfactorily with the experimental curve (see Fig. 2), with the exception that on the outside of the second maximum there are two intensity steps instead of one. Complete agreement of the theoretical and experimental curves is obtained when the large amplitudes of the vibrations of the unbonded pairs of atoms indicated above are taken into consideration; the corresponding curve 6 is shown in Fig. 2. Thus, the data obtained by successive approximation are in complete agreement with the data obtained by the radial distribution method.

Since the BOB angle is determined by interatomic distances for which there are no clear peaks on the radial distribution curve, it is difficult to solve the problem of the precise value of this angle. The following method was used to determine this angle. Using the successive approximation method with different values of this parameter, a theoretical intensity curve was constructed (without taking into account the vibrational factors), and the value of the angle BOB giving the best agreement of the I(s) curve with the experimental curve was determined. Inasmuch as the amplitudes of the thermal vibrations of the atoms were not taken into account, it is, of course, impossible to expect complete agreement of these curves: However, the agreement obtained was acceptable, and when the vibrational factors are taken into account in future calculations, it will be easier to obtain agreement of the theoretical and experimental curves. In this manner it was found that the angle BOB is approximately 95°, and we take this value as the most probable value without analyzing the possible error.

Thus, a planar B_2O_3 model with a linear arrangement of the O−B=O bonds and the following parameters:

1) $r(B - O) = 1{,}36 \pm 0{,}02$ Å;
2) $r(B = O) = 1{,}20 \pm 0{,}03$ Å;
3) $\angle BOB = 95°$.

agrees with our electron diffraction data.

It may be remarked that a B_2O_3 model of the type of (V) is in good agreement with the literature values for the boron−oxygen bond lengths. Within the limits of experimental error, the distance r(B−O) = 1.36 A agrees with the B−O bond length in boric acid esters, as determined by electron diffraction, and with the B−O bond length in boric acid, H_3BO_3, and its salts, as determined from x-ray data [14]. The distance r(B O) = 1.20 A agrees with the bond length in the BO molecule as determined from spectroscopic data [14]. The oxygen valence angle of 95° agrees with the experimental and theoretical values of the magnitude of this angle in compounds of similar type. The results of our investigation are in agreement with those obtained in an investigation of boric oxide vapors by infrared spectroscopy [15], which indicate a completely planar structure for the B_2O_3 molecule.

Our earlier investigation of the geometry of the B_2S_3 molecule [1, 3], which is a structural analog of the B_2O_3 molecule, confirms the interpretation and the results of this investigation of the boric oxide molecule by electron diffraction.

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* See English translation.
** See C.B. translation.

THE REACTION OF ALKYLCYCLOSILOXANES WITH TITANIUM TETRACHLORIDE

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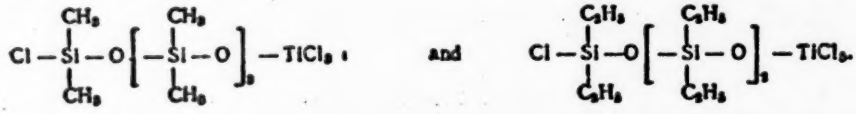
Cyclic organosilicon compounds are converted by the action of acid or basic catalysts to polymers [1-4]. Thus, the action of sulfuric acid on octamethylcyclotetrasiloxane yields a polydimethylsiloxane elastomer [5]. Octamethylcyclotetrasiloxane undergoes a similar conversion in the presence of bases.

In a study of the reaction of alkylcyclosiloxanes with titanium tetrachloride, we have found that octamethyltetracyclosiloxane and hexaethyltricyclosiloxane react with titanium tetrachloride at a temperature above 140°, the rings opening during the course of the reaction. The reaction proceeds according to the following scheme:

$$[R_2SiO]_n + TiCl_4 \rightarrow Cl\,[R_2SiO]_n\,TiCl_3.$$

In our investigation of the behavior of octamethyltetracyclosiloxane $[(CH_3)_2SiO]_4$ and hexaethyltricyclosiloxane $[(C_2H_5)_2SiO]_3$ in this reaction, we obtained the following compounds:

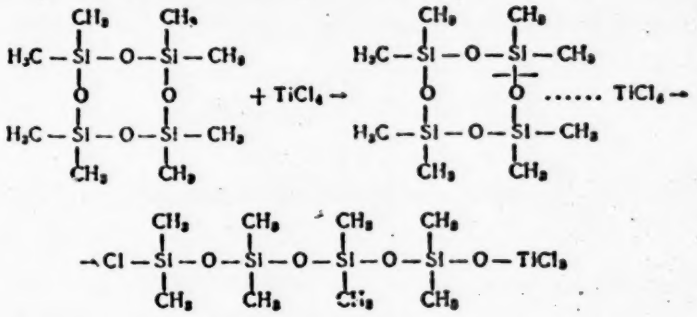


and

These new titanium-containing organosilicon compounds are pale-yellow liquids which are highly sensitive to atmospheric moisture. They darkened somewhat under the action of light during prolonged storage in glass vessels.

The reaction by which the compounds indicated above are formed takes place in the absence of catalysts; therefore, the reaction products are easily separated in a high degree of purity.

The mechanism of the reaction may be assumed to involve first the coordination of the oxygen atom of the siloxane bond with the titanium atom in titanium tetrachloride, which results in the formation of an unstable complex with a weakened silicon–oxygen bond. This results in cleavage of the ring, and one chlorine atom adds to the silicon at one end of the organosiloxane chain while the trichlorotitanium group adds to the other end of the chain. This process can be represented as follows (using as an example the interaction of titanium tetrachloride with octamethyltetracyclosiloxane):



This reaction may be used as a convenient method for the introduction of titanium into an organosiloxane molecule with a linear chain.

EXPERIMENTAL

The following compounds were used in the work: "Pure" grade, technical specifications 2553-51 titanium tetrachloride; octamethyltetracyclosiloxane with a b.p. of 32-34°/2 mm Hg and a molecular weight of 296.6; hexaethyltricyclosiloxane with a b.p. of 72-74°/2 mm Hg and a molecular weight of 312.1.

Reaction of Titanium Tetrachloride with Octamethyltetracyclosiloxane. The reaction flask, which was fitted with a stirrer, a reflux condenser, and a thermometer, was carefully dried and sealed from atmospheric moisture, and 80 g (0.27 mole) of octamethyltetracyclosiloxane and 52 g (0.273 mole) of titanium tetrachloride were charged to the flask. The reaction mixture was stirred and heated to 170°, and held at this temperature for 6 hours, after which it was cooled. The reaction product was distilled under vacuum from a flask fitted with a Vigreaux column, and 27 g of a product having the formula $Cl[(CH_3)_2SiO]_4TiCl_3$ was obtained; the product boiled at 97-98°/2 mm.

Found %: C 19.91; 20.19; H 5.41; 5.23; Ti 10.70; 10.85; Si 22.55; 22.54; Cl 28.08; 28.39 $C_8H_{24}Si_4O_4TiCl_4$. Calculated %: C 19.75; H 4.98; Ti 9.85; Si 23.09; Cl 29.15

Reaction of Titanium Tetrachloride with Hexaethyltricyclosiloxane. The reaction was carried out in a manner analogous to that described above, using 42.25 g (0.139 mole) of hexaethyltricyclosiloxane and 26.3 g (0.138 mole) of titanium tetrachloride. Vacuum distillation of the reaction product gave 16.5 g of a substance having the formula $Cl[(C_2H_5)_2SiO]_3TiCl_3$, and which boiled at 141-143°/2 mm.

Found %: C 30.32; 30.50; H 6.49; 6.48; Ti 10.3 (from total ash) Si 16.05; 16.06; Cl 29.33; 29.11 $C_{12}H_{30}SiO_3TiCl_4$. Calculated %: C 29.03; H 6.12; Ti 9.65; Si 16.97; Cl 28.57

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THE EFFECT OF POLYMERS CONTAINING CONJUGATED DOUBLE BOND SYSTEMS ON THE HEAT- AND LIGHT-STABILITY OF POLYVINYLCHLORIDE

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It can now be considered established that heat- and light-induced oxidative degradation of halogen-containing carbon-chain polymers proceeds by a radical chain mechanism [1]. This process is apparently initiated by radical products of the degradation of macromolecules, particularly, alkoxy and hydroxyl radicals, which arise during the decomposition of polymeric hydroperoxides [2, 3]. Chain propagation occurs as a consequence of the splitting off of hydrogen and halogen atoms, which results in dehydrochlorination, the accumulation of double bonds, and the decomposition of the macromolecule [1-3]. In spite of the fact that at the present time there is no unequivocal proof of the mechanism of the initiation, propagation, and termination of chains during heat- or light-induced oxidative degradation of polyvinyl chloride (PVC), it may nevertheless be asserted that the most effective inhibition of this process can be obtained only through the use of substances which are free radical acceptors. Naturally, radical acceptors are effective stabilizers for polymers only provided that when heated or irradiated in the presence of air they do not form hydroperoxides, which can initiate degradation processes.

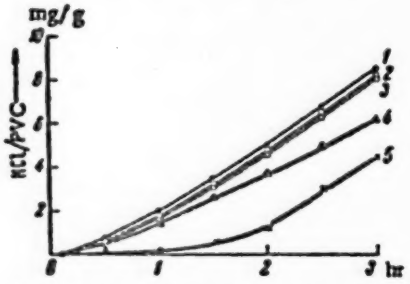

Fig. 1. Rate of dehydrochlorination of PVC at 175° in a stream of air: 1) without stabilizer; 2) with 1% lead silicate; 3) with 1% dibutyltin maleate; 4) with 1% diphenylolpropane; 5) with 1% PVC.

In this connection, it would be interesting to investigate the effect on the heat-induced oxidative degradation of polyvinyl chloride of certain types of recently synthesized polyphenylvinylenes (PPV) [4] and of products containing conjugated double bonds and obtained from the degradation of certain high polymers, particularly polyvinyl chloride.

The low activity of such quasiradicals is due to their ability to react only at comparatively high temperatures ($\geq$ 150-200°) [4]. An investigation of the electron paramagnetic resonance spectra of PPV and dehydrochlorinated PVC showed that in the ground state they contain a large number of unpaired electrons ($10^{17} - 10^{19}$ paramagnetic particles per gram); these are delocalized along the conjugated chain [5]. This circumstance suggests that such materials might be highly effective inhibitors of heat-induced oxidative degradation of halogen-containing polymers. Experimental data from the present investigation are presented in Table 1, and these data confirm that such materials are inhibitors.

TABLE 1

Stabilizer substance	No. of paramagnetic particles per g	Amt. of stabilizer, in % of PVC	Temp. of initiation of dehydrochlorination of PVC, °C	Duration of induction period to initial PVC dehydrochlorination, minutes	V, mg HCl/g PVC	$\frac{V}{V_0}\cdot 100$, %
PVC without stabilizer	—	—	158	7	3,91	100
Polyphenylvinylene (I)	$2,41\cdot10^{19}$	0,1	—	8,5	2,16	55
		1,0	158	7	1,34	34
		5,0	—	7	1,30	33
		10,0	—	5	1,43	37
Phenylacetylene–paradiethylbenzene copolymer (II)	$4,35\cdot10^{18}$	0,1	—	6	2,54	65
		1,0	153	7	2,53	65
		10,0	—	5	3,30	84
PVC-dehydrochlorination product (III)	$2,10\cdot10^{17}$	1,0	160	9	3,07	78
		5,0	—	8	2,41	65
		10,0	—	10	3,13	80

Note. The average integral rate of dehydrochlorination of PVC in the presence (V) and absence (V_0) of a stabilizer was determined at 175° in a stream of air; the duration of an experiment was 180 minutes. The ratio $(V/V_0)\cdot100$ characterizes the change in dehydrochlorination rate due to the presence of the stabilizer.

TABLE 2

Stabilizer	Amount of stabilizer, in % of PVC	Temp. at which dehydrochlorination rate was determined, °C	Duration of induction period to initial PVC dehydrochlorination, minutes	V, mg HCl/g PVC	$\frac{V}{V_0}\cdot 100$, %
PVC without stabilizer	—	175	7	3,91	100
		185	6	10,0	100
		195	5	20,7	100
Polyphenylvinylene (I)	1,0	175	7	1,34	34
	1,0	185	5	6,30	63
	5,0	185	6	6,20	62
	10,0	185	7	6,17	62
	1,0	195	3	19,0	92
	5,0	195	3	20,0	96
	10,0	195	3	20,8	100
PVC-dehydrochlorination product (III)	1,0	175	9	3,07	78
	1,0	185	8	7,8	78
	5,0	185	6	6,4	64
	10,0	185	7	9,0	90
	1,0	195	6	27,0	130
	5,0	195	5	20,7	100
	10,0	195	6	31,2	151

The PPV obtained by thermal polymerization of phenylacetylene at 150° (I) is an effective inhibitor of heat-induced degradation of PVC; the infusible and insoluble copolymer of phenylacetylene and paradiethylbenzene (II) prepared at 300° is less effective as an inhibitor, as is the product of the exhaustive dehydrochlorination of PVC under vacuum at 300° (III).

Figure 1 presents kinetic curves for the elimination of hydrogen chloride from PVC at 175° in the presence of various stabilizers; these curves show that product (I) possesses highly effective stabilizing action.

It should be noted that when large amounts of the insoluble products were used, their stabilizing effectwas decreased. In the case of the insoluble and infusible polymers with conjugated double bonds, contact of the radicals

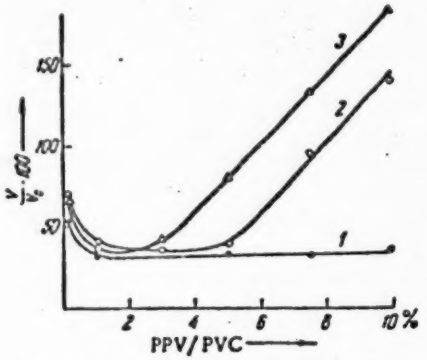

Fig. 2. Rate of dehydrochlorination of PVC at 175° in a stream of air in the presence of: 1) PPV prior to thermal treatment; 2) PPV after standing for 6 hours at 300°; 3) PPV after standing for 6 hours at 400°.

formed during the degradation of polyvinyl chloride with the active centers of the polymeric stabilizers was apparently difficult.

Table 2 presents data on the inhibiting effect of polyvinylenes I and III on the decomposition of PVC at different temperatures.

The data of Table 2 show that the effectiveness of polyvinylenes decreases at elevated temperatures. Product (I) inhibited the thermal decomposition of PVC at 185° and did not accelerate it at 195°. In contrast to (I) product (III) accelerated the degradation of PVC at 195°. This specific effect of product (III), which was prepared by dehydrochlorination of PVC, is apparently associated with the formation of active radicals during thermal cracking of the polymer. Such radicals can stick to the network of the dehydrochlorinated polymer and interact with oxygen with the formation of radicals which initiate degradation of PVC at elevated temperatures.

In this connection, it was of interest to determine the effect of thermal treatment of PPV (I) on its stabilizing effect. The experimental data show that when PPV is heated to 300 and 400°, there is an increase in the degree of conjugation, as indicated by a deepening of the color of the polymer from yellow to brown and black; at the same time, there is an increase in the concentration of unpaired delocalized electrons from $2.4 \cdot 10^{17}$ to $4.2 \cdot 10^{18}$ and $3.4 \cdot 10^{19}$ paramagnetic particles per gram, respectively [4]. Simultaneously, there is partial dehydrogenation of the polymer, as indicated by a decrease in hydrogen content from 6.12 to 5.88 and 5.16%, and the formation of radical centers is apparently possible. The data of Fig. 2 confirm the assumption of the possible fromation during thermal treatment of polyphenylvinylene of active radicals capable of initiating degradation of PVC. The original PPV remains an effective inhibitor over the concentration range of from 0.1 to 10% (by weight of PVC); it initiates degradation at concentrations of 8% and higher after treatment at 300°, and after it has been treated at 400°, initiation of degradation begins at a concentration of 6%.

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DETERMINATION OF THE HEAT CONTENT AND HEAT CAPACITY OF BERYLLIUM OXIDE OVER THE TEMPERATURE RANGE OF 1200 TO 2820°K

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The heat content and heat capacity of beryllium oxide have been measured by Magnus and Danz [1] over the temperature interval of 373-1175°K. (The results of Magnus and Danz were used in the tables of Kelly [2], who evaluated their accuracy at 3%.) The present article presents the results of an experimental determination of the heat content and heat capacity of solid beryllium oxide over the temperature interval of 1200-2820°K, i.e., up to the melting point. These measurements were carried out using the method of mixtures in a block calorimeter with an isothermal jacket. The samples were heated in a high-temperature vacuum furnace; the temperature of the sample was measured by means of a Model EOP-51M optical pyrometer with an accuracy of from 0.05-0.2%.

The beryllium oxide samples were pressed from a crystalline powder. The samples were pressed into the form of the containers, which had the shape of a truncated cone. A small amount of glucose (up to 0.1%) was added to bond the containers to the samples; the glucose burned during the course of the firing. The samples were fired at a temperature of 1400°C (preliminary firing) and then at a temperature of 1800°C (final firing). The BeO samples contained insignificant amounts (not exceeding a few hundredths of a percent) of a number of metals (Al, Ni, Cu, Zn, Hg, Fe, Ti, and others). After firing, the samples contained 99.9% BeO. The approximate weight of the samples was 35 g. Molybdenum and tungsten were selected as the materials for construction of the containers. According to the data of Jonson [3], the systems BeO–Mo and BeO–W do not react under vacuum at temperatures up to 2200-2300°K. We did not observe any interaction at even higher temperatures.

The determination of the heat content of beryllium oxide over the temperature interval of 1200-2400°K was carried out in molybdenum containers prepared from pure metal sheet which had a thickness of 0.2 mm. Tantalum proved to be unsuitable as a material for the containers (at temperatures above about 2300°K, a BeO sample in a tantalum container was covered with a gray deposit, which x-ray analysis showed to contain compounds of beryllium oxide with tantalum). Tungsten containers were used in the temperature interval of 2400-2820°K. Disadvantages of tungsten containers are their brittleness and their significant weight (the high heat content of the container increased the experimental error). The tungsten containers were also used for the determination of the heat of transition from the solid to the liquid phase; when so used, they were specially constructed so as to provide a completely hermetic seal for the inside of the container. The heat contents of the molybdenum and tungsten containers were determined by blank runs on the empty containers.

Table 1 presents the experimental values of the heat content of beryllium oxide; the measurements were made in the Kharkov State Institute of Standards and Measuring Instruments (KhGIMIP). The error of the heat

Expt. No.	T, °K	$H_T - H_{298.16}$ cal/mole	Expt. No.	T, °K	$H_T - H_{298.16}$ cal/mole	Expt. No.	T, °K	$H_T - H_{298.16}$ cal/mole
1	1142	8646	21	1813	17060	41	2278	23782
2	1169	9030	22	1838	17340	42	2310	24000
3	1208	9408	23	1864	17740	43	2329	24270
4	1242	9855	24	1889	18060	44	2334	24152
5	1276	10230	25	1915	18455	45	2408	25400
6	1286	10280	26	1925	18766	46	2432	25600
7	1336	10990	27	2002	19702	47	2475	26263
8	1344	11156	28	2035	19916	48	2526	27080
9	1358	11311	29	2054	20305	49	2566	28100
10	1418	12031	30	2065	20380	50	2637	28330
11	1443	12332	31	2084	20811	51	2646	28600
12	1471	12645	32	2102	21020	52	2672	28100
13	1475	12707	33	2119	21345	53	2697	29930
14	1511	13160	34	2126	21189	54	2820	40833
15	1522	13290	35	2142	21520	55	2822	40883
16	1595	14232	36	2155	21774	56	2840	40917
17	1646	14716	37	2164	22039			
18	1651	15308	38	2182	22065			
19	1684	15333	39	2297	22955			
20	1703	15562	40	2262	23100			

Note. Experiments from Nos. 1-44 were carried out in molybdenum containers; Nos. 45-53 were carried out in tungsten containers; in experiments Nos. 54-56 the samples were partially melted.

content measurements was 0.25% over the interval of 1100-2000°K and 0.5% over the interval above 2000°K. The coefficients of the interpolation equation were found by applying the method of least squares to the experimental data. The equations for heat content and heat capacity are:

The root mean square error of the determination of the coefficients of the equations presented above was 0.4% for experiments with tungsten containers it was 1.1%.

This is the first time heat content values of BeO have been measured at temperatures as high as those used in the present work. For this reason, comparison of the KhGIMIP data with those of other authors is possible only at temperatures to 1200°K. Heat content values calculated from the above equation, with an accuracy of 1%, agree with the results of Rodigina and Gomel'skii [4], which were obtained at the Sverdlovsk Branch of the VNIIM [All-Union Scientific Research Institute of Metrology], and they also agree with the data published by Kelly.

During the course of the work on the determination of the heat content, data were obtained on the melting point of BeO. According to our measurements, the melting point of beryllium oxide is 2820 ± 9°K.

Ya. L. Ol'shanskii obtained a value of 2843 ± 30°K for the melting point of beryllium oxide [5], and M. P. Slavinskii obtained 2793 ± 30°K.

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THERMODYNAMIC INVESTIGATION OF 1,1-DICYCLOHEXYLDODECANE, 1,1-DIPHENYLDODECANE, AND 1-PHENYL-1-CYCLOHEXYLDODECANE AT LOW TEMPERATURES

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The aim of the present investigation was the determination of certain thermodynamic properties of dicyclohexyldodecane, diphenyldodecane, and 1-phenyl-1-cyclohexyldodecane at standard conditions. All three substances were first purified chromatographically.* The dicyclohexyldodecane and diphenyldodecane were prepurified by zone melting [1]. Determination of the purity was carried out in a calorimeter by melting point depression using a method analogous to that described in reference [2]. The apparatus and the method and course of the c_p measurements have been described previously [3].

TABLE 1

Smoothed Heat Capacity Values, $c_p\left(\frac{\text{cal}}{\text{degree} \cdot \text{mole}}\right)$

Temp., °K	$C_{30}H_{60}$	$C_{30}H_{54}$	$C_{30}H_{56}$	Temp., °K	$C_{30}H_{60}$	$C_{30}H_{54}$	$C_{30}H_{56}$
10	1.561	1.430	1.38	191° solid 2	78.51	—	—
20	8.606	7.460	8.12	200	80.011	83.92	84.80
30	15.244	14.24	13.8	225	89.69	93.89	93.7
40	21.079	20.71	20.3	250	98.318	104.54	103.13
50	26.549	26.70	25.85	275	107.537	122.67	116.98
75	38.510	39.86	39.27	275.84° solid	—	125.00	—
100	49.066	49.05	49.95	275.84° liquid	—	143.00	—
125	56.525	57.23	58.5	281.4° solid	109.842	—	—
150	63.015	65.45	67.00	281.4° liquid	139.308	—	—
175	73.854	74.25	75.85	300	142.153	146.40	138.25
191° solid 1	82.71	—	—				

* By extrapolation.

The heat capacity of the empty calorimeter was measured at 47 points over the temperature interval from 12-320°K; the heat capacities of dicyclohexyldodecane, diphenyldodecane, and 1-phenyl-1-cyclohexyldodecane were measured at 69, 90, and 67 points, respectively.

The experimental values of the heat capacities were smoothed graphically and then tabulated over uniform temperature intervals (Table 1). The deviation of the experimental heat capacities from the smooth curve did not exceed 0.15%. No decline in heat exchange was observed over the entire temperature interval, which indicated that there was no sorption of the helium present in the calorimeter as a heat exchange gas.

* The compounds were synthesized in the Institute of Petrochemical Synthesis AN SSSR by A. A. Petrov and coworkers [4].

TABLE 2

Thermodynamic Properties at Standard Conditions

Compound	Formula	$H^\circ_{298.16} - H^\circ_0$, cal/mole	$S^\circ_{298.16}$, cal/deg·mole	H_m, cal/mole	S_m, cal/deg·mole	T_m °K	$c_{p\,298.16}$, cal/deg·mole	Purity, % mole
Dicyclohexyldodecane (s)	$C_{36}H_{70}$	19519±50	130.42±0.4	1058±50	35.20±0.15	300.58±0.02	134.46	98.2
1-Phenyl-1-cyclohexyldodecane (liq)	$C_{36}H_{66}$	30166±80	166.33±0.6	8406±50	30.51±0.15	275.84±0.02	146.06	97.6
Diphenyldodecane (liq)	$C_{36}H_{62}$	28672±80	163.70±0.6	9284±50	33.00±0.15	281.40±0.02	141.934	99.09

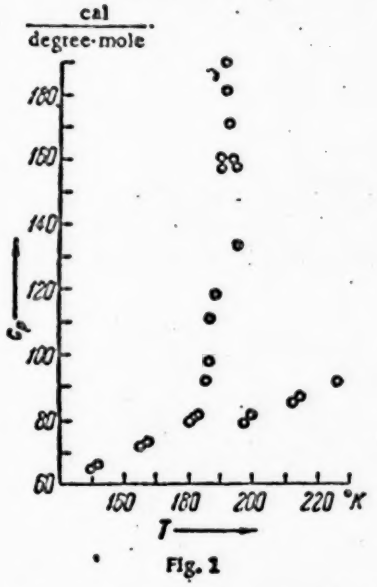

Fig. 1

Owing to the presence of impurities in the samples, melting began at lower temperatures and was apparent on the heat capacity curves 20 and 30° below the triple point. Therefore, in order to obtain the heat capacity of the solid in this region, the additional effective heat capacity was calculated from the smoothed values by means of the following equation

$$\Delta c_i = H_m \frac{T^\circ - T^s}{(T^s - T_i)^2},$$

where Δc_i is the effective increase in heat capacity due to melting of the impurities, T° is the triple point temperature, T^s is the melting point of the compound, T_i is the temperature at which the additional effective heat capacity was calculated, and H_m is the heat of melting.

In view of the fact that the heat capacities of dicyclohexyldodecane and 1-phenyl-1-cyclohexyldodecane did not obey Debye extrapolation ($c = aT^3$) at 13°K and higher, extrapolation to 0°K was accomplished graphically. This is quite acceptable, the more so since according to our evaluation, the absolute error in the entropy at 298.16°K (0.3-0.4 e.u.) due to the impurities in the sample was greater than the absolute value of the entropy at 15°K (0.2 e.u.). With these substances the Debye law is apparently followed only at lower temperatures.

The relationship between the temperature and the heat capacity of diphenyldodecane became cubic in the temperature range from 13 to 16°K: $c_p = 1.43 \cdot 10^{-3} T^3$. The heat capacity curve of this same substance had a peak in the temperature interval from 181-199°K; this was probably due to a phase transition associated with a change in the structure of the crystals (Fig. 1). The integral heat of the phase transition was:

$$H_{tr} = 460.7 \pm 1 \frac{\text{cal}}{\text{mole}}$$

The standard entropy and heat content were obtained by numerical integration of the c(T) and $\frac{c_p}{T}$ (T) curves. Values for these thermodynamic functions are presented for all three substances in Table 2.

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THE HYPOCHLOROUS ACIDIUM ION AS THE CHLORINATION AGENT IN AQUEOUS SOLUTION

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There is at present more than one opinion regarding the question of the significance of the hypochlorous acidium ion in the mechanism of chlorination in aqueous solution. We have earlier considered this problem [1, 2], and we found that the hypochlorous acidium ion, in contrast to the corresponding bromine and iodine cations, does not play an appreciable role in aqueous halogenation. We were also led to this same conclusion by the observation that the addition of strong acids (with the exception of hydrochloric) have little accelerating effect on the reaction of hypochlorous acid with organic compounds [3], even though the concentration of the hypochlorous acidium ion must increase proportionately with an increase in hydrogen ion concentration in accordance with the equation

$$HOCl + (H_3O)^+ \rightleftharpoons (ClOH_2)^+ + H_2O. \qquad (1)$$

The work of Soper and co-workers [4] also gave no indication of the participation of the hypochlorous acidium ion in reactions of hypochlorous acid, although these authors assumed this to be the case.*

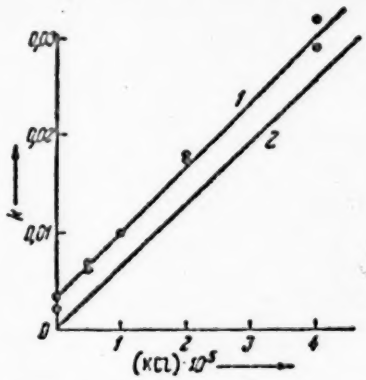
Several years ago, however, de la Mare, Hughes, Vernon, and Ketley [6, 7] proposed a theory according to which the hypochlorous acidium ion is the main active agent in the chlorination of organic compounds with dilute hypochlorous acid. The basis for this assertion was the observation that the rate of chlorination of anisole, phenol, mesitylene, and methyl meta- and paratolyl ethers is almost independent of the concentration of the organic compound and can be expressed by the equation:

$$-\frac{d[HOCl]}{dt} = k[HOCl] + k'[HOCl][H^+].$$

Hence, there arises an analogy with the nitration reaction, the rate of which is limited, under certain conditions, by the stage in which the nitronium cation is formed from nitric acid [8, 9]. The British authors proposed a similar dissociation of HOCl as a limiting stage of the chlorination reaction: $ClOH \rightleftharpoons Cl^+ + OH^-$ and $ClOH + H^+ \rightleftharpoons (ClOH_2)^+ \rightleftharpoons Cl^+ + H_2O$.

This assumes that the possibility of the formation of molecular chlorine is eliminated by the addition of silver salts.

* Derbyshire and Waters [5] observed a catalytic effect of strong acids on the reaction of hypochlorous acid with toluene-ω-sulfonic acid at very high catalyst concentration (1-4 M), and sulfuric acid was enormously more active than perchloric. It is possible that under these conditions, it is not the hypochlorous acidium ion that is formed, but acyl hypochlorites.



1) Linear plot of k; 2) linear plot of $k_R[H^+][Cl^-]$.

In 1952, we noted [10] that the decomposition of HOCl with the formation of the hypochlorous acidium ion is improbable, and that the rate of the reactions investigated by the British authors is apparently limited not by the rate of formation of the hypochlorous acidium ion but by the rate of rehydrolysis of chlorine from HOCl through the agency of the traces of chloride ion available in the solution. De la Mare and co-workers did not agree with our conclusions [7], and they referred to the fact that our experiments were carried out with more concentrated and less acidic solutions of HOCl that theirs. In the present article we present new evidence in support of our contention that the hypochlorous acidium ion has no significance in reactions of HOCl and that the kinetic relationships established in the work of de la Mare and co-workers [6, 7] are associated with the formation of molecular chlorine.

We selected anisole as the compound to be chlorinated, for it is distinguished by being easily chlorinated, while the action of HOCl on it is enormously weaker. We measured the rate of disappearance of active chlorine in mixtures containing, in addition to anisole, HOCl and nitric acid, and, in addition, small amounts of chloride ion (as KCl).

If it is assumed that the rate of chlorination of anisole, v, is determined by the rate of rehydrolysis of chlorine, then

$$v = k\,[\mathrm{HOCl}] = k_R\,[H^+]\,[\mathrm{HOCl}]\,[Cl^-]$$

and, consequently,

$$k = k_R\,[H^+]\,[Cl^-]. \qquad (2)$$

Values for the rate constant for the rehydrolysis of chlorine k_R have been determined by different methods [11]. As a probable average, we assume that $k_R = 6.5 \cdot 10^5$ liters$^2 \cdot$ mole$^{-2} \cdot$ min^{-1} (at 0°).

The experiments were carried out at 0° in blackened vessels. The hypochlorous acid was prepared by double distillation of an aqueous solution of chlorine and Ag_3PO_4. Solutions with a specific electrical conductance of $2 \cdot 10^{-6}$–$2.6 \cdot 10^{-6}$ ohm$^{-1} \cdot$ cm^{-1} at 0° were used for the kinetic experiments. Samples having a volume of about 5 ml were titrated with 0.01 N thiosulfate from a pneumatic buret. The chlorination reaction was very sensitive to traces of hydrochloric acid; therefore, the reproducibility of the experiments depended on the quality of the original preparations of hypochlorous acid. In each individual experiment, the first-order rate constants with respect to active chlorine were, in general, constant, although in certain cases, particularly in experiments in which KCl was not added, there was a noticeable tendency toward an increase in the rate constant during the course of the experiment.

By the data of Table 1, it is possible to establish that the chlorination rate depended somewhat on the anisole concentration*, and, in the presence of chloride ion, it was directly proportional to the hydrogen ion concentration. In the remainder of the discussion we shall use data from experiments where the hydrogen ion concentration was constant and the anisole concentration was as high as possible.

The figure compares experimental values of k for two series of experiments at different chloride ion concentrations with values of $k_R[H^+][Cl^-]$ at the same concentrations of reagents. The initial concentrations in all experiments were: anisole, 0.01 M; HNO_3, 0.001 M; HOCl, 0.001 M. In one series, the experiments were carried out with the same HOCl solution during the course of several hours of the same day.

* In de la Mare's experiments [7], the anisole concentration had almost no effect at all on the chlorination rate. It is possible that this divergence from our observations is explained by the different temperature (25°) used by the British authors for their experiments.

TABLE 1

$A \times 10^3$	2,5	5	10	2	10	2	10	10	10	10	2,5	10	10
$[HOCl] \times 10^6$	1	1	1	1	1	1	1	1	1	1	1	1	1
$(HNO_3) \times 10^3$	—	—	—	1	1	1	1	1	2	3			
$(NaOH) \times 10^3$											2	2	30
$(KCl) \times 10^6$	—	—	—	—	—	2	2	1	1	1	—	—	—
$k \times 10^2$	0,09	0,11	0,15	0,2	0,34	1,0	1,7	1,4	3,0	4,2	0,1	0,18	0,6

* A is the concentration of anisole; brackets denote the true concentration and parentheses the analytical concentration of the reagents at a temperature of 0°.

TABLE 2

	Series I				Series II						
$(AgCl) \times 10^6$	—	—	0,5	0,5	—	0,25	0,5	1	2	0,5	—
$(KCl) \times 10^5$	—	0,5	—	0,5	—	—	—	—	—	2	—
$k \times 10^2$	0,38	0,73	0,64	1,0	0,2	0,57	0,6	0,8	0,9	2,2	1,5
$(k - k_0) \times 10^2$	0	0,37	0,26	0,62	0	0,37	0,4	0,6	0,7	2,0	1,3
$k_R [H^+] [Cl^-] \times 10^2$	0	0,32	0,32	0,65	0	0,16	0,32	0,65	1,3	1,6	1,3

We note that the straight lines representing the dependence of chlorination rate (1) on chloride ion concentration and the line (2) representing the dependence of $k_R[H^+][Cl^-]$ on chloride ion concentration lie close to each other, and differ by a small, constant amount. It is further clear that even at very low chloride ion concentrations (of the order of 10^{-5} M), the chlorination of anisole occurs chiefly by molecular chlorine. Extrapolating the chlorination rate to zero addition of KCl, we find that k_0, the intercept on the ordinate, is equal to 0.003 minutes^{-1}. The experiments in which KCl was not added gave similar values.

The value of k_0 is composed of contributions from three sources: (a) chlorination of anisole by hypochlorous acid without the participation of chloride ion or hydrogen ion, (b) chlorination by traces of chlorine present in the initial HOCl solution, (c) chlorination by hypochlorous acidium ion insofar as it participates in the reaction.

We may find the contribution of reaction (a) by measuring the rate of chlorination of anisole in the presence of small additions of a base, when the concentrations of chloride and hypochlorous acidium ions are decreased to insignificant values. This method was complicated by the circumstance that the addition of small amounts of a base did not decrease, but increased the chlorination rate to a certain maximum at 25-30% neutralization of the HOCl*. By extrapolating the values of k to zero addition of base, we obtain k_a for reaction (a), 0.0015 min^{-1}. The difference $(k_0 - k_a)$, which is equal to 0.0015 min^{-1}, is the sum of the rate constants for (b) and (c). If all of the 0.0015 min^{-1} is due to molecular chlorine, then with the aid of the value of k_R it is possible to calculate the chloride ion content in our kinetic mixtures introduced with the initial hypochlorous acid. This calculation gives a value of $2.2 \cdot 10^{-6}$ M. It is quite possible, and even probable, that there was such a chloride concentration in our solutions. De la Mare and co-workers assumed that they freed their solutions from the presence of chloride ion by the addition of silver salts [6, 7, 12]. Apparently, they did not take into account that very disperse silver chloride can act like dissolved chlorine.

In order to evaluate the effect of very small concentrations of AgCl, we carried out the following experiments. A $4 \cdot 10^{-5}$ M solution of AgCl was prepared by mixing equimolar solutions of $AgNO_3$ and KCl, and AgCl solutions from $2 \cdot 10^{-5}$ to $0.5 \cdot 10^{-5}$ M were prepared from this solution by dilution. Thin layers of the $2 \cdot 10^{-5}$ M solution appeared turbid, while the less concentrated solution was completely transparent. These solutions of AgCl were introduced into the usual mixtures used in our kinetic experiments, sometimes with the addition of KCl. The silver chloride did not cause any appreciable decomposition of the hypochlorous acid in control experiments without anisole.

* This phenomenon finds explanation in the fact that the chlorinating agent in basic solutions is chlorine monoxide. Its formation from HOCl, which is the slow stage of the reaction, accelerates with the addition of a base, probably owing to the reaction $HOCl + OCl^- \rightleftharpoons HO^- + Cl_2O$ [3].

Table 2 presents values of the constant k from experiments in the presence of AgCl and, for comparison, values of $k_R[H^+][Cl^-]$. In all experiments, the temperature was 0°, and the concentrations were (in mole/liter): anisole, 0.005; HOCl, 0.001; HNO_3, 0.001. During the course of an experiment, the values of k display only an insignificant upward trend. The Cl^- concentrations may be taken as the sum of the AgCl and KCl concentrations.

The data of Table 2 show that AgCl exerts a significant catalytic effect on the chlorination of anisole by hypochlorous acid, an appreciable effect even with the addition of KCl to $2 \cdot 10^{-5}$ M. The close correspondence of $(k-k_0)$ with the values of $k_R[H^+][Cl^-]$ indicates that at low concentrations, silver chloride gives approximately the same catalytic effect as soluble chlorides. Therefore, our experiments on the addition of AgCl could not give the result which the British authors expected.

In general, the data of our new investigation, together with our previous observations [1,2], confirm that the hypochlorous acidium ion has no significance in the chlorination of organic compounds by hypochlorous acid in aqueous solutions, even in the absence of chloride ion. From a theoretical point of view, this conclusion finds explanation in the fact that the equilibrium in reaction (1) is extremely unfavorable for the formation of the hypochlorous acidium ion, or, in other words, that the basic properties of HOCl are extremely weak (cf. [5]). This conclusion is in agreement with thermodynamic calculations of the possible equilibria of the hypochlorous acidium ion with hypochlorous acid [13].

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PREPARATION OF METHYLPENTADIENES BY DEHYDRATION OF OXIDATION PRODUCTS OF PROPYLENE DIMER

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The present communication reports experimental data regarding the preparation of hexadienes with conjugated bonds by dehydration of the oxidation products of propylene dimer. Moreover, our investigations showed that the proposed method for the synthesis of alkadienes is more general and can be considered a universal method for the preparation of dienes from the olefinic hydrocarbons occurring in the liquid and gaseous products of petroleum processing.

The polymerization of propylene over solid phosphoric acid catalyst has found widespread industrial application in the production of alkylarylsulfonate-type detergents. During the polymerization of propylene, a considerable amount of propylene dimer is also formed along with propylene trimer and tetramer. Practical exploitation of propylene polymerization by industrial establishments has shown that the polymerization products contain up to 20% dimer. The reaction can be directed toward maximum dimer formation by changing the polymerization conditions.

The structure of propylene dimer has been a subject of investigation by a number of authors [1-5], who established that it is composed of hexenes of different structures. Without going into detail relative to the differences among individual authors as to the composition of the dimer, we may say that according to the best confirmed investigations, the dimer consists chiefly of 2-methyl-2-pentene, 3-methyl-2-pentene, and 4-methyl-2-pentene.

Hydrocarbons containing a double bond readily undergo liquid-phase oxidation at moderate temperatures with the formation of hydroperoxides [5-10]; in this case, the locations most vulnerable to oxidation are the carbon atoms occurring alpha to a double bond. As would be expected, the occurrence of a primary, secondary, or tertiary carbon in the alpha position leads to selective oxidation in the following order: tertiary > secondary > primary.

Hydroperoxides rapidly decompose in the presence of hot alkalies with the evolution of oxygen and the formation of unsaturated alcohols in yields up to 80% [8, 9]. Therefore, oxidation of olefins in the presence of an alkali should make it possible to combine the reaction by which hydroperoxides are formed with the reaction by which hydroperoxides decompose to yield unsaturated alcohols. Our experiments established that during oxidation of unsaturated hydrocarbons in the presence of alkaline reagents, other, side reactions take place leading to the formation of oxides and a very small amount of glycols, carbonyl compounds, and other oxygen-containing products.

Oxidation products prepared from propylene dimer by the method indicated above were used by us as the starting material for the synthesis of rubbery diene polymers; this represents the first such use of this material.

TABLE 1

Fraction	Boiling range, °C	Yield, wt. %	d_4^{20}	n_D^{20}	Mol. wt. found	Mol. wt. calc.	MR found	MR calc.
Hexene oxides	80 — 110	35,6	0,7986	1,4180	102	98	30,67	29,35
Hexenols	110 — 180	44,8	0,8539	1,4270	101	100	30,07	30,97
Glycols and other oxidation products	180 — 235	18,6	0,9466	1,4460	101	—	—	—
Residue		2,0						

TABLE 2

Initial fraction °C	Dehydration temperature °C	Run time, hours	Amount of 60-80° fraction in catalyzate, wt. %	Constants of 60-80° fraction d_4^{20}	Constants of 60-80° fraction n_D^{20}
		Hexene oxides			
80 — 110	340	1	94,2	0,7280	1,4240
	350	1	93,4	0,7284	1,4242
	360	1	93,8	0,7290	1,4244
	400	1	93,8	0,7284	1,4246
	350	2	93,6	0,7294	1,4246
	350	5	91,2	0,7286	1,4238
		Hexenols			
110 — 180	340	1	95,8	0,7316	1,4240
	350	1	95,6	0,7308	1,4238
	380	1	93,8	0,7310	1,4240
	350	5	91,5	0,7300	1,4240
		Oxides + hexenols			
80 — 180	350	1	95,6	0,7304	1,4244
	350	1	93,4	0,7296	1,4248
	350	5	92,3	0,7296	1,4246

EXPERIMENTAL

The starting material for the preparation of hexadienes was an oxidation product obtained by oxidation of propylene dimer with atmospheric oxygen at a temperature of 70-80° and a pressure of 15-20 atm. and in the presence of $NaHCO_3$ solution and small amounts of a catalyst (magnesium resinate) and an initiator (cumene hydroperoxide). According to unpublished data of N. N. Vorozhtsov, L. A. Ivanova et al., when the oxidation of the dimer is carried out for the purpose of subsequently synthesizing hexyl and heptyl alcohols, the hexene conversion is about 28-32% optimum conditions.

After decomposition of the peroxide compounds present in the oxidation products, the material had the following constants: d^{22}_4 0.8484; n^{22}_D 1.4280, mol. wt. 130; Engler distillation: i.b.p. 78°; 10%, 89°; 20%, 98°; 30%, 105°; 40%, 114°; 50%, 125°; 60%, 135°; 70%, 149°; 80% 171°; 90%, 225°; e.p. 234°.

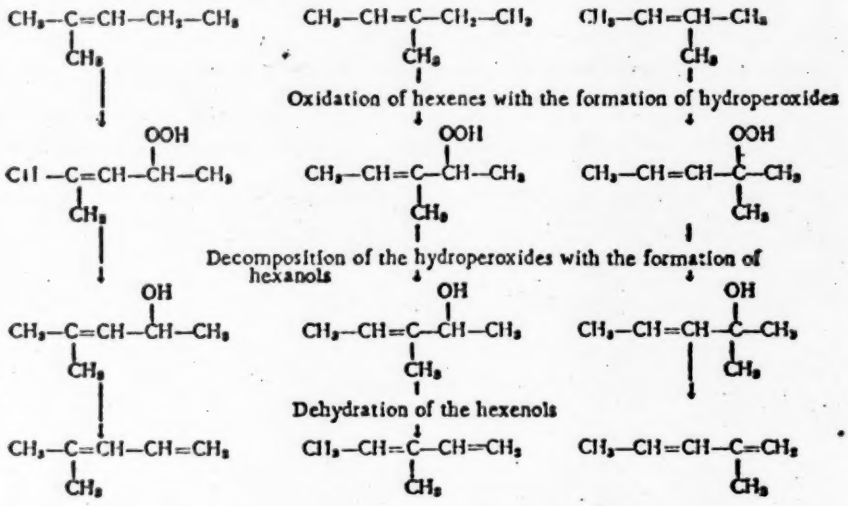
The oxidation products were fractionated into hexene, hexenol, and hexene oxide fractions (see Table 1).

The fractions corresponding to oxides and unsaturated alcohols, both individually and together, were subjected to dehydration over aluminum oxide. A catalyzate corresponding to the theoretical yield of dienes from the unsaturated alcohols and oxides present in the feed was obtained at temperatures of 350-400° and a space rate of 0.5-2 volumes of feed per volume of catalyst per hour. Results of individual experiments carried out at a space rate of 0.5 liter per liter of catalyst per hour are presented in Table 2.

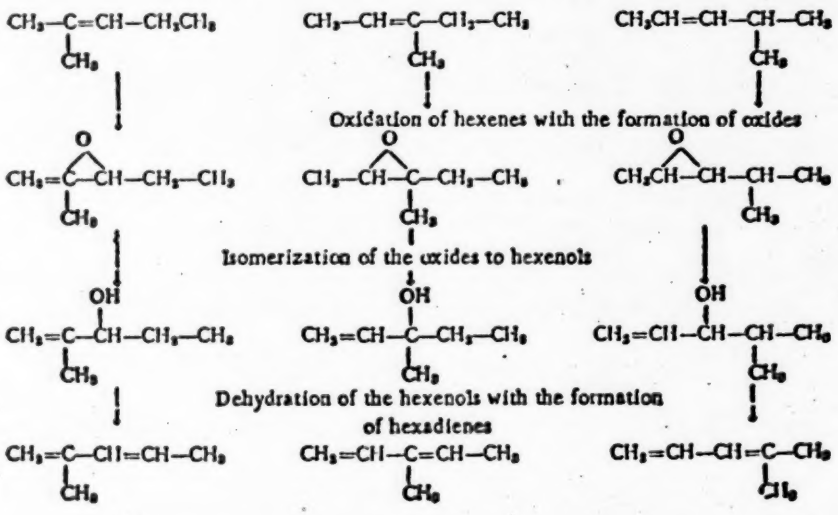
As may be seen from the data of Table 2, the amount of the 60-80° fraction in the catalyzate varied from 92-95%. Analysis showed that the 60-80° fraction contained from 70-80% diene hydrocarbons.

The formation of dienes from 2-methyl-2-pentene, 3-methyl-2-pentene, and 4-methyl-2-pentene, which are the major components of propylene dimer, can be represented as proceeding through the formation of hydroperoxides and unsaturated alcohols and through the formation of hexene oxides as in the following two schemes:

1. Formation of hexadienes through hydroperoxide and unsaturated alcohol stages.


Oxidation of hexenes with the formation of hydroperoxides
Decomposition of the hydroperoxides with the formation of hexanols
Dehydration of the hexenols

2. Formation of hexadiene through oxide and unsaturated alcohol stages.


Oxidation of hexenes with the formation of oxides
Isomerization of the oxides to hexenols
Dehydration of the hexenols with the formation of hexadienes

As may be seen from these schemes, successive conversion of the hexenes present in propylene dimer, both in the case of the first stage and in the case of the second stage, leads to the formation of three methylpentadienes with conjugated bonds, namely 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, and 4-methyl-1,3-pentadiene.

The catalyzate was copolymerized with butadiene and with styrene in an emulsion system, and latexes and rubbers having the required technical properties were obtained. The polymerizations were carried out with the kind cooperation of B. A. Dolgoplosk in the laboratory of the Scientific Research Institute of Synthetic Rubber.

Thus, we have developed a new process for the production of alkadienes with conjugated double bonds from unsaturated hydrocarbons.

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REPRESENTATION OF MULTICOMPONENT SYSTEMS BY MEANS OF MODELS

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In investigations of systems formed by three or four components, models are frequently used to depict more graphically the relationship between composition and properties than it can be accomplished by means of graphs. Models become still more useful with an increase in the number of components (and other conditions affecting equilibrium), since figures in n-dimensional space can be used to represent composition in this case. Thus, five-component systems of various types are mainly represented by means of three different four-dimensional figures [1]: 1) pentatope – for simple systems, i.e., systems formed by five metals or oxides or salts with a single common ion; 2) a tetrahedral hexahedroid – for reciprocal systems formed by four cations and two anions (or four anions and two cations), i.e., a system of eight simple salts; 3) a prismatic hexahedroid – for reciprocal systems formed from three cations and three anions, i.e., a system of nine simple salts. We shall denote these different types of five-component systems by, respectively: 5 ‖ 1; 4 ‖ 2; 3 ‖ 3.

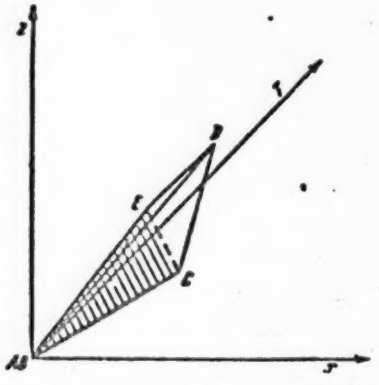

Fig. 1. Optimal model for depicting simple five-component systems (type 5 ‖ 1).

These four-dimensional figures can be projected on six coordinate planes. However, analysis shows that the resulting projections are not equivalent with respect to their descriptiveness and practical usefulness. In each case, only one of the planar projections, which we have named optimal projection [2], permits representation of all components on a uniform scale, gives a graphic representation of the boundaries of the individual phases of the system, and permits quantitative calculations.

Depending on the nature of the system and the properties of the four-dimensional figure, construction of the complete equilibrium diagram is accomplished by means of several projections of the optimal type: For the systems 5 ‖ 1; 4 ‖ 2, and 3 ‖ 3, respectively, three four, and nine optimal projections are used. It is possible, however, to project the figures enumerated above in three-dimensional space rather than on a plane. By referring them to a cartesian coordinate system with x, y, z and T axes, it is possible to prepare projections of the model in four-coordinate space; xyz, xyT, xzT, and yzT. Like the projections of this same figure on planes, these space projections also differ from each other with respect to their descriptiveness.

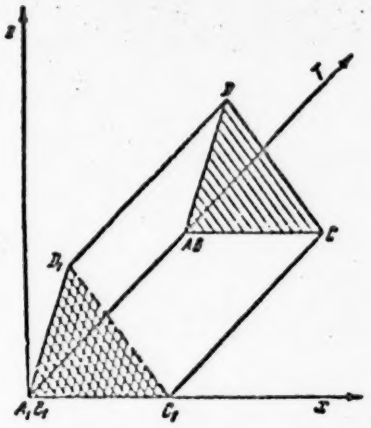

Fig. 2. Optimal model for representation of reciprocal systems of five components forming eight simple salts (type 4 ‖ 2).

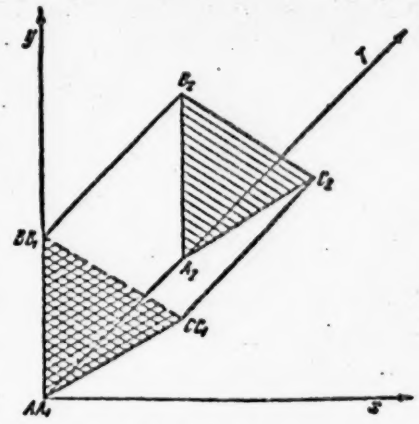

Fig. 3. Optimal model for representation of reciprocal systems of five components forming nine simple salts (type 3 ‖ 3).

It has been found that only the projection in xzT space is optimal for the pentatope (see Fig. 1). This projection is a tetrahedron, three of the corners of which correspond, respectively, to three components of the system (E, D, and C), while the fourth corner represents the sum of the remaining components (A and B). In order to reflect the equilibrium diagram of the 5 ‖ 1 system in its entirety, it is necessary to construct two models of the type of Fig. 1.

For the tetrahedral hexahedroid, there is also only one projection permitting quantitative calculations – the projection in xzT space (see Fig. 2). This projection is a triangular prism; four of its corners, D, C, D_1 and C_1 (two in the upper and two in the lower base), correspond to four of the simple salts of the system, while the remaining two corners each represent the total of a pair of the remaining salts (AB and A_1B_1). Thus, in order to represent a 4 ‖ 2 system in its entirety, it is necessary to construct two models of the type of Fig. 2, since the original system forms eight simple salts. Finally, the prismatic hexahedroid can be projected in two coordinate systems, xyT and xzT. The models of these two cases are similar. One of them is shown in Fig. 3.

The original nine simple salts are distributed as follows on the triangular prism: three salts (A_2, B_2, C_2) at the corners of the upper base, and the remaining six in pairs at the three corners of the lower base (AA_1, BB_1, and CC_1). Therefore, in order to represent the complete equilibrium diagram of a 3 ‖ 3 system, it is necessary to construct three models of the type of Fig. 3. The models shown in Figs. 1, 2, and 3 can be constructed on the basis of data regarding the composition of the ternary systems represented on the faces of the tetrahedron or on both prisms. At the same time, preliminary equilibrium diagrams of the corresponding five-component systems will be obtained, and these will provide an orienting idea of the five-component system as a whole.

Such models are very useful for forecasting compositions having desirable properties and for indicating the most promising directions for investigations of multicomponent systems.

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THE FREE-RADICAL ADDITION OF MONOBASIC ACIDS AND THEIR METHYL ESTERS TO α-OLEFINS

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It has previously been shown that ethylene undergoes telomerization with isobutyric acid at a temperature of 250°and a pressure of 850-950 atm, with the formation of a mixture of telomeric homologs of α,α-dimethylcarboxylic acids [1]. Other acids having a C— H bond at an alpha carbon atom may be used in this reaction.

The present communication presents a description of the synthesis of dialkylacetic acids by means of the free-radical addition of straight-chain acids to alpha olefins. The reaction of propionic, butyric, enanthic, and capric acids (or their methyl esters) with 1-hexene, 1-octene, 1-decene, and 1-tridecene were studied in the present work; these reactions proceed according to

$$R-CH_2-COOH + CH_2=CH-R' \rightarrow R'-CH_2-CH_2-CH(R)-COOH.$$

The addition of isobutyric acid to decene showed that this method can also be used for the synthesis of trialkylacetic acids. The reaction was carried out at atmospheric pressure and in the temperature interval of 135-180°; tert-butyl peroxide served as the initiator. Table 1 presents the experimental conditions, the amounts and mole ratio of the components of the reaction and of the peroxide, and the structures and yields of the addition products (1:1 adducts). The properties of the products obtained — acids and esters — are presented in Table 2. Experiments I-VII and IX were carried out under standard conditions: The original acid (or its methyl ester) was charged to the flask, and the olefin and peroxide were added dropwise over a period of 5-7.5 hours. The acid was taken in five- to eight-fold excess with respect to the olefin. The data of Table 1 show that 1:1 adducts were formed in rather high yields (36-69%) in practically all cases. The lowest yield, that of dimethylhexylacetic acid (experiment III), may be explained by the insufficiently high reaction temperature. The methyl esters of the acids (experiments VI and IX) formed 1:1 adducts in yields somewhat lower than those obtained with the acids. The amount of peroxide had a substantial effect on the yield of addition product. In two experiments carried out under the same conditions at mole ratios of methyl enanthate to 1-octene to peroxide of 7.7:1.0:0.26 and 7.7:1.0:0.13, the yield of the methyl ester of amyloctylacetic acid was 56.5% in the first case and 40% in the second. Replacement of the continuous method of feeding peroxide to the reaction zone by a portionwise method also led to a decrease in the yield of 1:1 adduct from 56.5% (experiment VI) to 42.4% (experiment VIII). In addition to the 1:1 adducts, high-molecular-weight products were also formed in all cases.

When tert-butyl peroxide is used as the initiator, the free radical reactions usually take place at temperatures not below 120°. In the reaction described above, advantage was taken of the fairly high boiling points of the original acids or esters to attain such temperatures. When the reaction was carried out using the methyl esters of propionic, butyric, and isobutyric acids (which do not have sufficiently high boiling points), the addition to the alpha olefins could be accomplished only in an autoclave. Table 1 presents the conditions used in the autoclave

TABLE 1

Expt. No.	Reaction product	Reaction components		Amount used in the reaction						Temp. °C	Time, hours	Yield based on olefin %	
		acid or ester A	olefin B	A		B		peroxide				used	consumed
				g	mole	g	mole	g	mole				
			Experiments at atmospheric pressure										
I	n-$C_{12}H_{27}CH(CH_3)COOH$	C_3H_5COOH	Tri-decene	92,5	1,25	45,5	0,25	6,0	0,041	130—140	6,5	38,3	46,5
II	n-$C_{10}H_{21}C(CH_3)_2COOH$	$(CH_3)_2CHCOOH$	Decene	211	2,4	44,5	0,317	12,0	0,082	142—144	5,0	36,2	44,0
III	n-$C_6H_{13}C(CH_3)_2COOH$	$(CH_3)_2CHCOOH$	Hexene	211	2,4	26,5	0,315	12,0	0,082	120—130	5,0	12,1	24
IV	n-$C_9H_{19}CH(C_2H_5)COOH$	n-C_3H_7COOH	Hexene	211	2,4	26,5	0,315	12,0	0,082	130—150	5,5	69,5	—
V	n-$C_8H_{17}CH(C_6H_{11})COOH$	n-$C_6H_{13}COOH$	Octene	312	2,4	35,0	0,312	12,0	0,082	167—180	5,7	65	—
VI	n-$C_8H_{17}CH(C_6H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	6,0	0,041	150—152	5,0	56,5	—
VII	n-$C_8H_{17}CH(C_6H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	3,0	0,02	156—165	5,0	40	—
VIII	n-$C_8H_{17}CH(C_6H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	7,0	0,048	140—150	7,5	42,4	—
IX	$(n\text{-}C_6H_{17})_2CHCOOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	447	2,4	35	0,312	12,0	0,082	143—149	6	53,7	—
			Autoclave experiments										
X	n-$C_6H_{13}CH(CH_3)COOCH_3$	$C_3H_5COOCH_3$	Hexene	130	1,48	18,4	0,218	7,5	0,052	160—165	9,5	31,4	—
XI	n-$C_{10}H_{21}CH(CH_3)COOCH_3$	$C_3H_5COOCH_3$	Decene	130	1,48	20,7	0,148	7,2	0,049	160—170	22	30,8	37,2
XII	n-$C_{10}H_{21}C(CH_3)_2COOCH_3$	$(CH_3)_2CHCOOCH_3$	Decene	130	1,28	18	0,128	6,3	0,043	160—170	24	26,2	36
XIII	n-$C_6H_{13}CH(C_2H_5)COOCH_3$	n-$C_3H_7COOCH_3$	Hexene	153	1,5	13	0,15	7,5	0,052	155—160	23	34	
XIV	n-$C_9H_{19}CH(C_2H_5)COOCH_3$	n-$C_3H_7COOCH_3$	Hexene	160	1,57	13	0,15	7,5	0,052	118—150	9	17,7	

TABLE 2

Expt. No.	Addition product	Mol. wt. found**	Mol. wt. calc.	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Calc., % C	Calc., % H	M.p. of amide, °C
1*	n-$C_{12}H_{27}CH(CH_3)COOH$	258,5	256,42	173—174/3***					74,92	12,61	74,94	12,58	
2*	n-$C_{10}H_{21}C(CH_3)_2COOH$	229,5	228,37	142—144/3****									94—95
3*	n-$C_9H_{19}C(CH_3)_2COOH$	171,9	172,26	102—103/3,5	0,9022	1,4350	49,82	50,17					102—103
4	n-$C_8H_{17}CH(C_2H_5)COOH$	174,9	172,26	107—108/4	0,8431	1,4344	49,09	50,17					
5*	n-$C_8H_{17}CH(C_6H_{11})COOH$	244,8	242,4	170—171/4	0,8845	1,4457	73,03	73,41	73,93	12,21	74,32	12,48	
6	n-$C_8H_{17}CH(C_6H_{11})COOCH_3$	258,2	256,42	94,5—95/1	0,8642	1,4370	77,73	78,18	74,93	12,20	74,94	12,58	
7*	$(n\text{-}C_8H_{17})_2CHCOOCH_3$	294,6	298,5	150—151/4	0,8619	1,4422	91,67	92,12	76,95	12,71	76,45	12,83	123—123,5
8	n-$C_9H_{19}CH(CH_3)COOCH_3$	174,0	172,26	60—62/5	0,8703	1,4210	50,19	50,29					
9*	n-$C_{10}H_{21}CH(CH_3)COOCH_3$	229,1	228,38	86,5—90/1	0,8661	1,4332	68,56	68,88					75,5—76
10	n-$C_{10}H_{21}C(CH_3)_2COOCH_3$	243,2	243,41	97—98/3	0,8708	1,4378	73,40	73,40					
11*	n-$C_8H_{17}CH(C_2H_5)COOCH_3$	186,4	186,3	68—72/6	0,8660	1,4248	54,98	54,94					100—101

* Literature data: 1) b.p. 172-173° (2.5 mm), m.p. 24° [3]; 2) b.p. 184° (12 mm), m.p. 27°, m.p. of amide 95-96° [4]; 3) m.p. of amide 103° [5]; 5) b.p. 181-184° (2-3 mm) [6]; 7) m.p. of amide 122.5-123.5° [7]; 9) m.p. of amide 77° [8]; 11) m.p. of amide is given in the present article.

** Molecular weights calculated from saponification and neutralization numbers.

*** M.p. 27-33°.

**** M.p. 23-27°.

experiments (Nos. X-XIV), while Table 2 presents the properties of the 1:1 adducts, the yields of which were 17-31%. In these experiments, the peroxide was introduced in three portions as a solution in a mixture of olefin and ester. Attempts were made to carry out the addition of methyl acetate to 1-decene, but these were unsuccessful. The experiments were carried out at different ratios of 1-decene to methyl acetate to peroxide in the temperature interval of 160-240°. Consequently, only those acids (and their esters) which have CH_2 and CH groups can be added to olefins. However, it would be expected that when several methylene groups are present in the molecule of acid, addition to an olefin would take place not at just the alpha C—H bond alone. In order to clarify this problem, the product of the addition of methyl butyrate to 1-hexene was saponified to the acid, with b.p. of 93-95° (2 mm), n^{20}_D 1.4336, and the acid was converted to the amide with a m.p. of 100.5-101° C. By means of alternate synthesis

$$C_4H_{11}CHO + C_2H_4MgBr \xrightarrow{H_2O} C_4H_{11}CH(OH)C_2H_4 \xrightarrow{HBr}$$
$$\rightarrow C_4H_{11}CHBrC_2H_4 \xrightarrow[2.\ CO_2]{1.\ Mg} C_4H_{11}CH(C_2H_4)COOH$$

we prepared ethylhexylacetic acid with a b.p. of 126-128° (5 mm) d^{20}_4 0.8957; n^{20}_D 1.4332. Its amide melted at 100-101°, and a mixture of this amide with the amide of the addition product melted without depression of the melting point. Had methyl butyrate added to the hexene by the beta carbon atom, 3-methylnonanoic acid would have been formed. The amide of 3-methylnonanoic acid was prepared from 2-bromooctane by malonic ester synthesis, and this compound was found to melt at 79°, which corresponds to the melting point given in the literature for this amide [8]. Thus, free radicals arising through the decomposition of tert-butyl peroxide remove a hydrogen atom only from the alpha carbon atom of the acid, which leads to the formation of the R—$\dot{C}$H—COOH radical which then adds to the olefin. The reaction proceeds by a chain mechanism. Experiments I-VII and IX were carried out under the same conditions. We shall confine ourselves to a description of one of them.

Experiment V. A mixture of 72 g of enanthic acid, 35 g of 1-octene, and 12 g of peroxide was added dropwise, over a period of 5 hours and 40 minutes and with vigorous stirring, to 240 g of enanthic acid heated to 180°, and the reaction mixture was heated for an additional hour. Owing to the formation of low-boiling products from the decomposition of the peroxide, the temperature of the mixture dropped to 167° toward the end of the experiment. The product was distilled to obtain 7.6 g of low-boiling products, 280 g of enanthic acid, 49 g of amyloctylacetic acid (65% yield), and 19.5 g of high-boiling residue. In experiment I, the reaction of propionic acid with 1-tridecene gave methyltridecylacetic acid, and distillation of the high-boiling residue yielded an acid with an m.p. of 51-53°, apparently having the following structure:

$C_{13}H_{27}CH(C_{11}H_{23})CH_2CH(CH_3)COOH$ (2:1 adduct)
Found %: C 79.60; 79.64; H 13.04; 13.32 $C_{29}H_{58}O_2$. Calculated % 79.38; H 13.32

In experiment VIII, 174 g of the ester, 13.5 g of 1-octene, and 2 g of peroxide were heated in a flask at 150° for 1 hour; the remaining peroxide and olefin were then added in five equal portions over equal time intervals.

Experiments X-XIV were carried out in a 200-ml steel autoclave without agitation; the ester and olefin were charged to the autoclave, and the tert-butyl peroxide was added in three equal portions: $^1/_3$ at the beginning of the experiment and $^2/_3$ at approximately equal time intervals (about 8 hours in XI-XIII and about 3 hours in experiments X and XIV). In experiments XI-XIII, the peroxide was added to the cold autoclave all three times, while in experiments X and XIV, $^1/_3$ of the peroxide was added to the cold autoclave and $^2/_3$, in solution in the ester, was injected into the autoclave at reaction temperature.

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ON THE REVERSIBILITY OF THE REACTION OF BETA-SPODUMENE WITH POTASSIUM SULFATE

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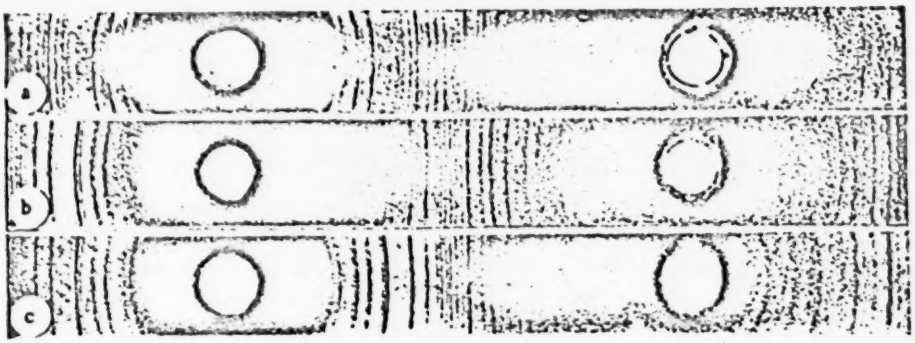
During the course of a study of the interaction of spodumene with sulfates of the alkali metals (Me_2SO_4), it has been established [1] that the clearly demonstrated ability of the beta modification of this mineral to react at high temperatures with various salts is generally not characterized by a tendency of the mineral toward decomposition into a series of phases with the formation of soluble aluminates and silicates. Over the course of the intersection of β-spodumene with Me_2SO_4, which takes place under many experimental conditions as a solid-phase process, there arises only a single new water-insoluble mineral formation; in addition, Li_2SO_4 is obtained, usually containing as an impurity Na_2SO_4 due to the isomorphic sodium present in the spodumene. It is precisely this circumstance which makes β-spodumene a convenient starting material for experimental mineralogy. Thus, by sintering β-spodumene with K_2SO_4, Rb_2SO_4, and Cs_2SO_4, we synthesized, respectively, leucite, rubidium aluminosilicate, and pollucite [1] having the composition $Me[AlSi_2O_6]$. Complete identification of these synthetic aluminosilicates has now been accomplished [2-5]. Only in the case of the interaction of β-spodumene with Na_2SO_4 was there observed decomposition of the mineral, vitrification of the mass, and finally, cessation of the reaction.

The formation of synthetic aluminosilicates also takes place during the interaction of α-spodumene with Me_2SO_4 [1]; however, it proceeds through an intermediate α→β transition of the spudomene, which requires an increased source of heat [6].

The data from x-ray investigation [1, 3-5] have shown that in the synthesis of alkali metal aluminosilicates from β-spodumene, a temperature of 900-950° is sufficient, and only if it is desired to force the reaction to completion (preparation of completely single-phase products) is it expedient to carry out the sintering at 1000-1050°.

It is also well known from the practice of the sulfate method of processing spodumene, which is based on sintering of this material with K_2SO_4 at 1050-1100°, that temperature has an effect on the degree of extraction of lithium by the sulfate, i.e., on the completeness of the transition of β-spodumene to leucite. The amount of K_2SO_4 charged to the sintering stage is no less significant. Although the amount of Li_2O in the spodumene concentrate is usually taken into account in evaluating the charge of K_2SO_4, this evaluation is, nevertheless, empirical. Since there is no quantitative information on the degree of extraction of sodium from spodumene during the sintering process, technological calculations are virtually independent of the basic reaction, which determines the mechanism of the interaction of the mineral with K_2SO_4. In many cases, weight ratios of the components of the charge of 1:1, or close to it, are used in composing the charge during operations with standard raw materials.

For a further study of the interaction of spodumene with K_2SO_4, an evaluation of the reagent charged in connection both with the extraction of the major (lithium) and minor (sodium) elements appeared of interest. As a



Debye patterns: a) original β-leucite; b) β-spodumene (standard); c) synthetic β-spodumene.

matter of fact, if spodumene were purely a lithium mineral, the reaction involved in sintering of the material with K_2SO_4 could be written in the following manner:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + K_2SO_4 = Li_2SO_4 + K_2O \cdot Al_2O_3 \cdot 4SiO_2. \quad (1)$$

In actuality, spodumene contains a variable amount of sodium, and, therefore, the basic reaction determining the mechanism of the interaction of the mineral with K_2SO_4 should be written in the form of a general equation:

$$(Li, Na)_2O \cdot Al_2O_3 \cdot 4SiO_2 + K_2SO_4 = (Li, Na)_2SO_4 + K_2O \cdot Al_2O_3 \cdot 4SiO_2. \quad (2)$$

In order to trace the nature of the extraction of lithium and sodium from spodumene experiments were carried out at different ratios of reaction components and over a broad range of temperature. The starting material was β-spodumene containing 5.44% Li_2O and 3.20% Na_2O [1]. The method of preparing the charge, the sintering, the water treatment of the sintered products, and the analysis of the solutions were similar to those described previously [2]. The sintering time was three hours in all cases. The results obtained by analysis of solution obtained by water treatment of the sintered products are presented in the table. In the table the amount of K_2SO_4 charged the sintering reaction, which comprised 20, 40, 60, 80, and 100% by weight of the β-spodumene, is expressed in percent of that theoretically required by reaction (1), and are compared with that according to reaction (2). The calculated data for reaction (2) are shown in parentheses.

As may be seen from the data in the table, the extent to which sodium went into the soluble phase is associated with the extent to which the lithium was made soluble, and there was a sharp increase beginning at 900°C, at which temperature, leucite, resulting from the interaction of β-spodumene with K_2SO_4 is detected in the reaction products [1, 2]. However, the relative amount of sodium extracted into the soluble phase gradually lagged behind the amount of lithium extracted from the spodumene. When the amount of K_2SO_4 charged was 250% of that required by reaction (2), extraction of lithium from the spodumene was practically complete, and at the same time there was considerable, but incomplete, extraction of sodium. A part of the latter was retained by the leucite formed during the sintering. Thus, the major part of the K_2SO_4 charged was used in the complete extraction of the lithium, and a certain amount was lost by the accompanying extraction of sodium, prevention of which does not appear possible.

The nature of the effect of excess K_2SO_4 on the degree of lithium extraction suggests that the reaction between β-spodumene and K_2SO_4 at high temperatures is reversible. The simplest way to confirm this assumption appeared to be to attempt to carry out the reverse synthesis of β-spodumene from leucite. With this aim, a sample of natural leucite (K_2O, 20.73; Na_2O 0.37, Al_2O_3 23.38; SiO_2, 55.46 wt. %) was sintered with lithium sulfate at ratios of 1:1 and 1:2 by weight (which comprised 340 and 680%, respectively) and at temperatures of 800, 900, and 1000° for periods of two and three hours. The method was completely analogous to that used for the synthesis of leucite [1, 2]. After all of the soluble salts had been washed from the sintered products, the material was subjected to x-ray analysis. The presence of β-spodumene was detected in all of the samples, and the products obtained from the experiments carried out at 900 and 1000° were single-phase, i.e., they were β-spodumene; leucite was not present.

Data on the Interaction of β-Spodumene with Potassium Sulfate

Reaction temp. °C	K_2SO_4 charged, based on reaction (1) or (2)(in % of theoretical)									
	62.5 (50)		125 (100)		187.5 (150)		250 (200)		312.5 (250)	
	Put into solution (in % of initial mineral)									
	Li_2O	Na_2O	Li_2O	Na_2O	Li_2O	Na_2O	Li_2O	Na_2O	Li_2O	Na_2O
700	—	—	—	—	trace	trace	1.68	2.84	2.74	4.69
800	trace	—	3.02	trace	4.82	4.38	6.74	7.83	8.19	9.83
900	6.15	trace	22.16	12.02	42.18	20.93	58.16	30.56	69.11	38.12
950	8.02	2.50	30.24	16.52	48.23	27.54	65.02	39.06	77.93	46.96
1000	9.42	6.94	36.51	23.90	59.12	40.04	77.30	50.34	89.11	61.07
1050	11.87	10.08	38.56	26.49	63.10	43.48	79.48	55.03	95.20	65.25
1100	14.04	11.15	49.13	32.62	73.40	45.94	88.05	59.36	96.24	70.33

One of the products which was prepared at 1000° and a reactant ratio of 1:1, was studied in greater detail. Silicate analysis gave (in wt. %): 7.97 Li_2O, 27.38 Al_2O_3, and 64.63 SiO_2. Calculated for $Li[AlSi_2O_6]$ (in wt. %): 8.04 LiO_2, 27.40 Al_2O_3, and 64.56 SiO_2. The average index of refraction was $n' = 1.519 \pm 0.003$; polymorphism, which is characteristic of leucite, was absent. The interplanar distances and intensities found by the powder method were in good agreement with the data recently obtained for β-spodumene [7]. The figure shows Debye patterns of the original leucite, β-spodumene obtained from natural α-spodumene by calcination at 1000° for six hours, and the synthetic β-spodumene obtained from the leucite. Thus, the synthesis of β-spodumene by the action of Li_2SO_4 on leucite is an established fact; this serves as proof of the reversibility of the basic reaction of the sulfate method of processing spodumene. This reaction can obviously be described by the following equation:

$$2\beta\text{-}Li[AlSi_2O_6] + K_2SO_4 \xrightleftharpoons{Q\,cal} 2\alpha\text{-}K[AlSi_2O_6] + Li_2SO_4. \qquad (3)$$

We may remark that the analogous route for the synthesis of β-spodumene from pollucite, $Cs[AlSi_2O_6]\cdot nH_2O$, and Li_2SO_4 failed in its purpose, which indicates a high stability of the bonds in the compound $Cs[AlSi_2O_6]$.

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LIQUID-PHASE ALKYLATION OF BENZENE WITH PROPYLENE OVER SILICA—ALUMINA AT LOW TEMPERATURES (+20, +50, +80°)

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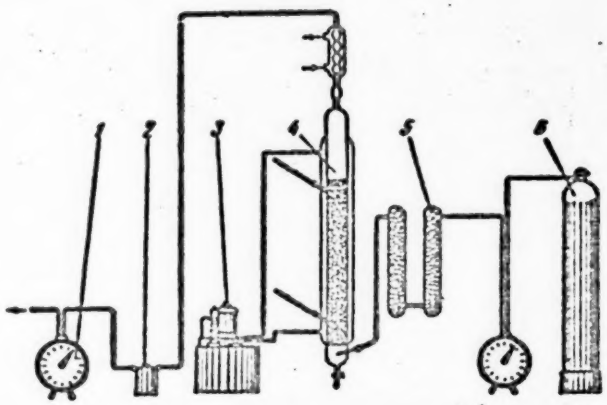
A number of catalysts have been used for the alkylation of aromatic hydrocarbons with olefins, of which the most widely used are:

1. Acids — hydrogen fluoride, sulfuric acid, phosphoric acid, compounds of boron trifluoride such as boron trifluoride hydrate, and molecular compounds of boron trifluoride with phosphoric acid. 2. Metal halides — aluminum chloride, zinc chloride, and others. 3. Synthetic and natural silica-aluminas.



Flow-type alkylation apparatus: 1) gas meter; 2) surge tank; 3) ultrathermostat; 4) reactor; 5) drier; 6) propylene cylinder.

Alkylation of aromatic hydrocarbons with olefins in the presence of acid catalysts is carried out at relatively low temperatures from 20-50°; with phosphoric acid deposited on a carrier as the catalyst, the temperature ranges from 180-200° at a pressure of 15-20 atm, while with aluminum chloride the temperature ranges from 50-80°.

It is well known [1-4] that alkylation over natural and synthetic silica-aluminas takes place under the following conditions. Hydrated silica-alumina: 250-400° and 25-40 atm; silica + clay: 400° and 100 atm, 380° and 5 atm, 350° and 35 atm; synthetic silica-alumina: 350-380° and 30 atm.

TABLE 1

Compositions of Mixtures of Alkylbenzenes (in mole percent) Obtained by Alkylation of Benzene with Propylene in the Presence of Different Catalysts ($C_6H_6 : C_3H_6 = 1:1$ at 50°)

	Equilibrium $AlCl_3$ [7]	Silica-alumina*	$AlCl_3 \cdot HSO_4$ **	$H_3PO_4 \cdot BF_3$ **
Monoisopropylbenzene	70.0	53.2	57.5	83.5
Diisopropylbenzene	24.0	36.7	24.0	10.5
Triisopropylbenzene	4.6	7.8	10.2	4.9
Tetraisopropylbenzene	1.5	2.3	8.3	1.1
Benzene content of crude alkylate (before fractionation)	34	49	36.4	14.8

* Space rate 35 $hours^{-1}$

** Space rate 10-20 $hours^{-1}$

TABLE 2

Yields of Alkylbenzenes (in percent of theoretical) from Alkylation of Benzene with Propylene in the Presence of Different Catalysts ($C_6H_6 : C_3H_6 = 1:1$ at 50°)

Alkylbenzene	Silica-alumina	$H_3PO_4 \cdot BF_3$	$AlCl_3 \cdot HSO_4$	$AlCl_3$
Monoisopropylbenzene	29.3	67	31	46-57
Diisopropylbenzene	26.6			
Triisopropylbenzene	6.7	22	46	26
Tetraisopropylbenzene	3.4			

The kinetics of the vapor-phase alkylation of benzene with propylene over silica-alumina at 325° and atmospheric pressure have recently been studied. Thus, the use of comparatively high temperatures and, in the majority of cases, high pressure is peculiar to alkylation over silica-alumina.

In the present work, the authors were the first to show that alkylation of aromatic hydrocarbons with olefins is possible in the liquid phase at relatively low temperatures, +20, 50, and 70°, at rates comparable with those obtained with an acid catalyst.

Experiments on alkylation over commercial silica-alumina were carried out in a vertical reactor (Fig. 1) having a diameter of 34 mm. The reactor was packed with a 68-cm layer of catalyst spheres; the catalyst volume was 450 ml, and the weight was 300 g. The activity index of the catalyst was 34, the BET surface was 305 m^2 per g, and the pore volume was 0.501 cc/g. The propylene, dissolved in the benzene charge (230 g), was fed into the lower part of the column. The olefin feed to the alkylator was a propane-propylene fraction containing 83% propylene and 17% propane. Alkylation in the presence of liquid acid catalysts was carried out in a three-neck flask fitted with a stirrer; the method has been described in previous communications [6]. The alkylation products were processed in the usual manner, and were distilled into fractions with boiling ranges corresponding to those of mono-, di-, tri-, and tetraisopropylbenzenes.

Monoisopropylbenzene and diisopropylbenzene were obtained in almost equal amounts over silica-alumina, but appreciable amounts of tri- and tetraisopropylbenzenes were also obtained. For purposes of comparison, Table 1 presents results from the alkylation of benzene with propylene in the presence of $AlCl_3$, $AlCl_3 \cdot HSO_4$ and $H_3PO_4 \cdot BF_3$. Although the product composition obtained with silica-alumina differed from those obtained with the other

TABLE 3

Compositions (in wt. %) of Alkylbenzenes Obtained by Alkylation of Benzene with Propylene in the Presence of Silica-Alumina at Different Temperatures (space rate 35 hours^{-1})

Alkylbenzene	At 20°	At 50°	At 70-80°
Monoisopropylbenzene	33	44	54
Diisopropylbenzene	49	41	25
Triisopropylbenzene	10	11	16
Tetraisopropylbenzene	8	4	5

Propylene conversion was 60%

TABLE 4

Physicochemical Properties of the Alkylbenzenes Obtained by Alkylation over Silica-Alumina at 20-50°

Property	Isopropylbenzene*		
	mono-	di-	tri-
B.p., °C	154 (152,5)	206—216**(206)	220—240***(239)
d_4^{20}	0,862 (0,862)	0,8604 (0,8608)	0,8619
$n^{20}D$	1,4905 (1,4913)	1,4899 (1,4898)	1,4922
Mol. wt.	120 (120)	162	202
Bromine No.	0	0	0

* Literature values of the constants are shown in parentheses.

** The major part boiled at 204°.

*** The major part boiled at 239°.

catalysts in that larger amounts of di- and polyisopropylbenzenes were formed, nevertheless the alkylation rate was the same or higher.

The yield of alkylbenzenes was high over silica-alumina; moreover, mono- and diisopropylbenzenes were formed in approximately equal amounts (see Table 2).

Table 3 presents the results of experiments on the alkylation of benzenes with propylene over silica-alumina at 20, 50, and 70-80°. With an increase in temperature, the yield of monoisopropylbenzene increased, and the yield of diisopropylbenzene decreased.

Table 4 presents the physicochemical constants of the alkylbenzenes obtained by alkylation over silica-alumina. The physicochemical properties of the alkylbenzenes corresponded to the literature values, and the alkylbenzenes did not contain polymer.

The possibility of alkylating benzene with propylene, with high yields at relatively low temperatures, is obvious if one considers the free energy of the formation of isopropylbenzene at atmospheric pressure according to the reaction:

$$C_6H_6 + C_3H_6 \rightleftarrows C_6H_5-C_3H_7,$$
$$\Delta F = -23378 + 34{,}01T.$$

ΔF has a high negative value at relatively low temperatures.

Silica-alumina is an acid catalyst, and a number of reactions take place both at low and at high temperatures in its presence; the reactions apparently proceed by a carbonium ion mechanism. Olefin polymerization is one of the low-temperature reactions. Thus, isobutylene polymerizes over natural silica-aluminas over a broad temperature range beginning at −80°.

It is well known that in a number of cases polymerization and alkylation reactions take place in the presence of analogous catalysts and under closely similar conditions. The low-temperature alkylation of benzene with propylene over silica-alumina catalysts is one of these reactions.

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o-HYDROXYBENZENESULFINIC ACID – A NEW ANALYTICAL REAGENT AND STRUCTURAL ANALOG OF SALICYLIC ACID

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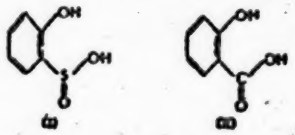
Sulfinic acids can be considered analogs of carboxylic acids. The use of aromatic sulfinic acids as analytical reagents is more suitable in a number of cases than is the use of aromatic carboxylic acids; sulfinic acids dissolve more readily in water, they precipitate certain metals from more acid media, and they possess a more selective action than the carboxylic acids [1-4].

It thus appeared to be of interest to synthesize and to study the analytical behavior of o-hydroxybenzene sulfinic acid (I) – a structural analog of salicylic acid (II).



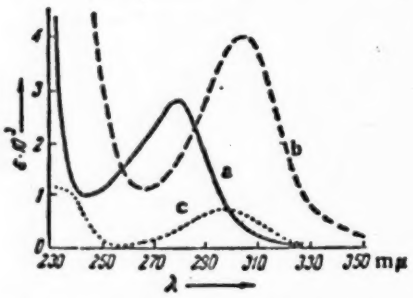


Fig. 1. Absorption spectra of aqueous solutions of o-hydroxybenzenesulfinic acid and of salicylic acid: a) un-ionized form of (I) (at a pH of 6); b) ionized form of (I) (at a pH of 11.98); c) un-ionized form of II (at a pH of 6; values of ε_{II} have been multiplied by a factor of 10).

This acid, which was prepared for the first time in the course of the present work, forms colorless prismatic crystals which are readily soluble in water. The material had a melting point of 71° after recrystallization from ether. Analysis showed that the percentage content of sulfur in this compound corresponded to that required by theory.

The absorption spectra of this acid were obtained at various pH values (see Fig. 1, which shows only two of the curves obtained for I and, for comparison, a curve for II), and on the basis of these curves the value of K_{OH} – the apparent dissociation constant of the OH group of this reagent – was determined. The sulfinic acid group apparently dissociates completely in solution, since the concentration of hydrogen ions in an accurately prepared 0.01 M solution of o-hydroxybenzenesulfinic acid was $1.38 \cdot 10^{-2}$ g-ion H^+ as measured by a glass electrode, which corresponds to a pH of 1.86; therefore, the isobestic point method, which was used for the determination of K'_{OH}, was inapplicable to the determination of the dissociation constant of the SO_2H group.

TABLE 1

pH	H^+	D	D_0	K'_{OH}	$K'_{OH\,av}$
8,34	$4,57\cdot10^{-9}$	0,075	0,0125	$2,29\cdot10^{-8}$	
9,15	$7,08\cdot10^{-10}$	0,125	0,0125	$6,37\cdot10^{-9}$	
9,55	$2,82\cdot10^{-10}$	0,150	0,0125	$3,10\cdot10^{-9}$	$7,15\cdot10^{-9}$
9,65	$2,24\cdot10^{-10}$	0,165	0,0125	$2,93\cdot10^{-9}$	(pK'_{OH} =
10,38	$4,17\cdot10^{-11}$	0,200	0,0125	$6,26\cdot10^{-10}$	= 8,15)

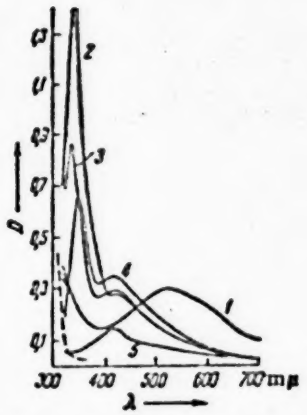


Fig. 2. Absorption curves of solutions of the complex of Fe^{3+} with I at different pH values (continuous lines). 1) pH 1.9 to 7.53; 2) pH 8.34; 3) pH 8.57; 4) pH 8.71; 5) pH 9.02. Concentration of iron, $2.041\cdot10^{-4}$ mole/liter; cell thickness, 1.00 cm; concentration of I, 0.04%. (The absorption spectrum of the reagent is shown by the broken line).

The determination of K'_{OH} by this method [5, 6] was accomplished by solution of the two equations:

$$D = D_0\left(1 + \frac{K'_{OH}}{[H^+]}\right) \quad \text{and} \quad K'_{OH} = \frac{D - D_0}{D_1 - D}[H^+],$$

where D_1, D_0, and D are the optical densities of, respectively, solutions containing molecules of this acid with ionized and un-ionized OH groups and a mixture of molecules in the ionized and un-ionized forms, and $[H^+]$ is the molar concentration of hydrogen ions in the solution containing a mixture of ionized and un-ionized molecules. The average value of K'_{OH} was calculated from five values obtained by means of the modified equation:

$$K'_{OH} = \frac{D - D_0}{D_0}[H^+].$$

The data are presented in Table 1.

By analogy with II, it would be expected that o-hydroxybenzenesulfinic acid would form characteristic compounds with a number of metals, especially with Fe^{3+}.

Absorption spectra were obtained for complexes of o-hydroxybenzenesulfinic acid with Fe^{3+} (see Fig. 2). It may be seen from Fig. 2 that the first, violet complex (λ_{max} = 523-527 mμ) exists over a broad pH interval of 1.9-7.53 (the pH region below 1.9 was not investigated); the strongly absorbing second complex (λ_{max} = 336-337, 345 mμ) exists in the narrow pH interval of 8.34-8.71, and occurs in equilibrium with the third complex (λ_{max} = 406-410 mμ) which is formed over the pH interval of 8.34-9.02. The solution was turbid at pH values above nine, which may be due to decomposition of the complex and formation of $Fe(OH)_3$.

By means of the Ostromyslenskii – Job method, we were able to establish that at a pH of 1.9 the mole ratio of reagent to Fe^{3+} is 1:1 in the violet complex (the measurements were carried out at 500 mμ and 415 mμ). At a pH of six and above, the components of the buffer mixture caused turbidity, and the mole ratio could not be established owing to the formation of acetate complexes of iron under these conditions. Similarly, Foley and Anderson [7] found it impossible to use this method to establish the mole ratio of Fe^{3+} and sulfosalicyclic acid in complexes formed in alkaline buffered solutions. Taking into account that at a pH of 1.9, dissociation of the OH group must be completely suppressed while the sulfinic acid group, on the contrary, is completely ionized and reactive under these conditions, we consider that the composition of the violet complex can probably be expressed by the formula:

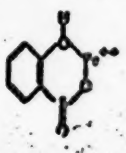


TABLE 2

Acid	Sequence number of complex	pH interval of existence of complex	λmax	ε max	Sensitivity, γ per ml
o-Hydroxybenzenesulfinic acid	1	1,9—7,53	523—527	1440	0,4
	2	8,34—8,71	336—337,345	6960	0,08
	3	8,34—9,02	406—410	1620	0,35
Sulfosalicylic acid	1	0,7—2,0	497	1800*	0,3*
	2	4,8—5,8	464	4300*	0,13*
	3	above 8	427	5750*	0,1*

* Calculated from literature data [8].

Upon comparing the data from spectrophotometric studies of complexes of o-hydroxybenzenesulfinic acid and of salicylic (or sulfosalicylic) acid [8-11] with Fe^{3+} (see Table 2), it is possible to observe an analogy in the behavior of these acids: they form three complex compounds with Fe^{3+}, and the absorption maxima of the first and third complexes almost coincide; the ratio of reagent to Fe^{3+} in the first, violet complex is the same, and the sensitivity of the reaction is of the same order.

The stability of the violet complex of (I) with Fe^{3+} (several days) and also the compliance of solutions of the complex with the absorption laws even in the interval of rather low concentrations, 0.18-0.9 γ Fe^{3+} per ml, suggest the use of this reagent for the quantitative determination of iron.

o-Hydroxybenzenesulfinic acid forms soluble complexes with certain metals, mainly in an alkaline medium, among which are colored complexes: orange-red with the uranyl ion, brown with cobalt, yellow-brown with nickel, and emerald-green with copper. It seemed of interest to consider the reaction of U(VI) with this reagent. We obtained a curve showing the pH dependence of the optical density of a solution of the complex of uranium with (I) (Fig. 3), on which there were two fairly well expressed maxima. The assumption of the existence of two complex compounds of U(VI) with o-hydroxybenzenesulfinic acid in weakly acid (pH 6.56) and weakly basic (pH 8.71) media was confirmed when absorption curves were obtained for solutions of the complexes at these pH values (the maximum in the absorption curve of the first complex was at 326 mμ, while that in the second curve was at 362 mμ).

The sensitivity of the reaction of our reagent with uranium at a pH of 8.71 in borate-buffered solution is 1.4 γ U per ml. Compliance with the absorption law also exists in the concentration interval of 2-50 γ U per ml, and this interval can be used for the quantitative determination of uranium. The sensitivity of the reaction with sulfosalicylic acid is 7 γ U per ml [12].

Finally, it should be noted that the presence of the sulfinic acid group in this reagent brings about the formation of insoluble precipitates with Ti, Zr, Th, U(IV), Sc, Bi, and certain other metals. The behavior of the yellow-orange precipitate of o-hydroxybenzenesulfinic acid with Ti is especially interesting: it is not extracted by organic solvents, but it is soluble in those which are miscible with water and which contain an alcohol group. The precipitates formed by the remaining cations enumerated above do not possess this property. The absorption curve of a solution of the complex of Ti with (I) at a pH of 1-2 in ethyl or isopropyl alcohol at a ratio of 1:1 (optimum reaction conditions) has a maximum at λ = 329-330 mμ (ϵ_{max} = 1160). The sensitivity of this reaction (0.4 γ Ti per ml), the compliance with the absorption law over the concentration interval 3.5-50 γ Ti per ml, and the stability of the complex over a period of time (12 hours) suggest the use of this reaction for the quantitative determination of Ti. A few words concerning the compound of Ti with this organic substance in 96% H_2SO_4 will be of interest. It is well known that salicylic acid forms a red color with Ti under these conditions. We were persuaded that this reaction would occur with all phenols and compounds with an enol group, including β-naphthol and 8-hydroxyquinoline (this can be used as a qualitative reaction for an enol group). o-Hydroxybenzenesulfinic acid alone in 96% H_2SO_4 is colored blue (qualitative reaction for the sulfinic group), but in the presence of Ti, the color changes to red.

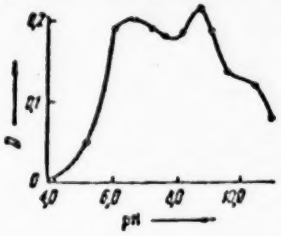


Fig. 3. Curve showing the dependence of D of a solution of the complex of UO_2^{2+} with (I) on pH. Uranium concentration, $1.68 \cdot 10^{-4}$ mole/liter.

Considering these results and comparing the properties of o-hydroxybenzenesulfinic acid with those of salicylic acid, including their behavior with the cations of certain metals, it is possible to form certain conclusions of definite theoretical interest. This new organic compound retains almost all of the chemical properties characteristic of II, but in contrast to salicylic acid, it reacts with a number of metals in more acid media, which is an advantage when the compound is used for analytical purposes. Analogous precipitates are formed by salicylic acid in an acid medium, but they decompose instantaneously with the precipitation of the free acid. A special property of the sulfinic acid group – existence in two tautomeric forms [13] – increases the dissociation constant of this acid and at the same time provides for the formation of compounds in an acid medium. o-Hydroxybenzenesulfinic acid differs rather sharply from salicylic acid with respect to its physical properties: its melting point is approximately half as great as that of salicylic acid; it is more soluble in water; its fluorescence is scarcely visible; it has less tendency toward sublimation (sublimes only under vacuum); the sulfinic acid group of this acid dissociates completely and the pK' of its OH group is 8.15, while the pK' of the carboxylate group of salicylic acid is 3 and the pK' of the OH group is 13.4 [11]. The similarity of the chemical properties of these acids emphasizes the very real analogy in their structures, while the differences in their physical properties can be explained by the ability of the sulfinic acid group to occur in two equilibrium forms with four- and six-valent sulfur atoms.

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THE REACTION OF TITANIUM TETRACHLORIDE WITH HEXAMETHYLDISILOXANE

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A number of methods for cleaving the siloxane bond have been described in the literature; these include the action of sulfuric acid [1-3], bases [4, 5], and $AlCl_3$ [6] on hexamethyldisiloxane. Our experiments have shown that cleavage of the siloxane bond with the formation of trimethylsiloxane derivatives of titanium takes place when titanium tetrachloride is allowed to act on hexamethyldisiloxane at temperatures exceeding 100°.

During the investigation of cleavage of the siloxane bond in hexamethyldisiloxane by titanium tetrachloride, it was found that if the process is carried out at temperatures of 120-200°, the reaction takes place according to the scheme

$$TiCl_4 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_3Ti[OSi(CH_3)_3] + (CH_3)_3SiCl;$$

the reaction yields only trimethylchlorosilane and trimethylsiloxytitanium trichloride (in 69.8% yield).

All attempts to obtain products of higher degrees of substitution, such as bis(trimethylsiloxy)titanium dichloride, were unsuccessful. However, when the reaction temperature was increased to 280-350°, bis(trimethylsiloxy)titanium dichloride was formed in accordance with the reaction

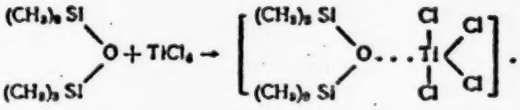
$$TiCl_4 + 2(CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_2Ti[OSi(CH_3)_3]_2 + 2(CH_3)_3SiCl.$$

The yield of bis(trimethylsiloxy)titanium dichloride was 34.7%. This shows that the replacement of a halogen attached to titanium by a second siloxy group probably proceeds as a result of the interaction of trimethylsiloxytitanium trichloride with hexamethyldisiloxane. In order to confirm this supposition, experiments were carried out in which trimethylsiloxytitanium trichloride was allowed to act on hexamethyldisiloxane at temperatures of 280-320°. Bis(trimethylsiloxy)titanium dichloride was formed under these conditions (in a yield of 43.0%) in accordance with the reaction

$$Cl_3TiOSi(CH_3)_3 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_2Ti[OSi(CH_3)_3]_2 + (CH_3)_3SiCl.$$

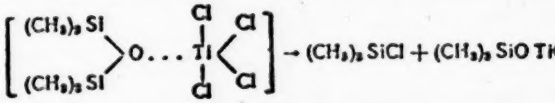
We consider that the rupture of siloxane bonds in hexamethyldisiloxane by titanium tetrachloride proceeds by the following mechanism.

The titanium atom of the titanium tetrachloride coordinates with an oxygen of the hexamethyldisiloxane with the formation of the transition complex



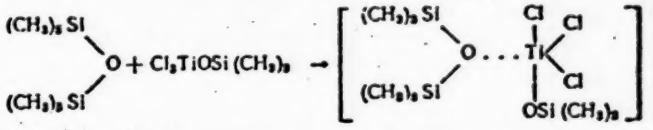
(I)

The remainder of the process, which takes place as a result of redistribution of the electron density, entails rupture of the siloxane bond with addition of the titanium to the oxygen and the formation of trimethylchlorosilane and trimethylsiloxytitanium trichloride:



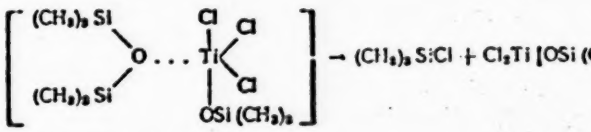
(II)

The addition of a second siloxy group to the titanium atom probably also proceeds through coordination of the titanium atom of the trimethylsiloxytitanium trichloride to hexamethyldisiloxane:



(III)

with the subsequent formation of trimethylchlorosilane and bis(trimethylsiloxy)titanium dichloride:



(IV)

EXPERIMENTAL

Preparation of Trimethylsiloxytitanium Trichloride. A mixture of 58.6 g (0.308 mole) of $TiCl_4$ and 50.0 g (0.308 mole) of hexamethyldisiloxane was charged to a Favorskii flask fitted with a long dephlegmator. The mixture was heated at a temperature of 120° for an hour, and the trimethylchlorosilane, 29.6 g (32.4% Cl) was then distilled at a temperature of 58-60°. The kettle residue was vacuum distilled at a temperature of 62-63°/8 mm (literature value, 67°/9 mm), and 52.52 g of trimethylsiloxytitanium trichloride was obtained for a yield of 69.8%.

Found %: Cl 43.56; 43.20 $C_3H_9OSiTiCl_3$. Calculated %: Cl 43.71

Preparation of Bis(trimethylsiloxy)titanium Dichloride. 1) A mixture of 29.0 g (0.153 mole) of $TiCl_4$ and 50.0 g (0.306 mole) of hexamethyldisiloxane was passed through a quartz tube packed with glass chips; the tube was heated by a furnace. The furnace temperature was 350°. The mixture which collected in the water-cooled receiver was subjected to fractionation. A total of 15.6 g of bis(trimethylsiloxy)titanium dichloride was collected at a temperature of 87-88°/8 mm. The yield was 34.7%.

Found %: C 24.49; H 6.36; Si 18.8; Ti 16.40; Cl 23.5 $C_6H_{18}O_2Si_2TiCl_2$. Calculated %: C 24.15; H 6.04; Si 18.8; Ti 16.45; Cl 23.88.

2) Similarly, but at a furnace temperature of 320°, 20.5 g of bis(trimethylsiloxy)titanium dichloride was separated by fractionation (at 63°/3mm) from the products of the reaction of 29.1 g (0.16 mole) of trimethylsiloxytitanium trichloride and 25.9 g (0.16 mole) of hexamethyldisiloxane. The yield was 43.0%.

Found %: Si 18.2, Ti 15.95; Cl 24.6 $C_6H_{18}OSi_2TiCl_2$. Calculated %: Si 18.8; Ti 16.45; Cl 23.88

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LIQUID-PHASE OXIDATION OF NAPHTHENIC HYDROCARBONS IN THE PRESENCE OF BORIC ACID

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The liquid phase oxidation of paraffinic and olefinic hydrocarbons in the presence of boric acid has previously been investigated in our laboratory [1, 2]. It was demonstrated that the structure of the hydrocarbon molecule has an effect on the nature of the oxidative conversion. In this connection, it seemed of considerable interest to study the oxidation of naphthenic hydrocarbons under conditions which would ensure that the process would be highly selective with respect to the formation of alcohols.

TABLE 1

Hydrocarbon	Found			Literature values [3]		
	b.p., °C/mm	n_D^{20}	d_4^{20}	b.p. °C/mm	n_D^{20}	d_4^{20}
n-Amylcyclohexane	77—78°/10	1,4449	0,8045	77/10	1,4445	0,8040
n-Heptylcyclohexane	109—110°/10	1,4492	0,8101	109/10	1,4486	0,8100
n-Nonylcyclohexane	138—139°/10	1,4530	0,8172	138/10	1,4522	0,8170

TABLE 2

Hydrocarbon	Hydroxyl No.	Acid No.	Ester No.	Carbonyl No.
n-Amylcyclohexane	87.0	5.6	9.0	18.2
n-Heptylcyclohexane	62.0	3.1	4.2	12.5
n-Nonylcyclohexane	89.6	5.8	6.2	15.8

For this purpose, a series of naphthenic hydrocarbons having side chains of different lengths (n-amylcyclohexane, n-heptylcyclohexane, and n-nonylcyclohexane) was synthesized via the Grignard route. The constants of these hydrocarbons are presented in Table 1.

Oxidation of the naphthenic hydrocarbons was carried out using a nitrogen-oxygen mixture containing 3.5% O_2 as the oxidizing gas; reaction conditions included a reaction temperature of 165°, normal pressure, a feed rate

TABLE 3

Alcohol	Found			Calculated
	b.p., °C/mm	n_D^{20}	hydroxyl number	hydroxyl number
$C_{11}H_{23}O$	81—82°/1	1.4668	321	329
$C_{13}H_{26}O$	99—101°/1	1.4680	280	283
$C_{15}H_{30}O$	119—121°/1	1.4683	240	248

TABLE 4

Alcohols	Alcohol contents, mole %	
	primary	secondary
$C_{11}H_{22}O$	2.7	97.3
$C_{13}H_{26}O$	2.2	97.8
$C_{15}H_{32}O$	1.5	98.5

of oxidizing gas of 1000 liters/kg·hour, and a run time of four hours. Boric acid was added in an amount of 5%.

The oxidation was carried out in an apparatus which we have previously described [1].

At the conclusion of an experiment, the oxidate was washed with hot water and analyzed. Characteristics of the oxidates are presented in Table 2.

TABLE 5

Hydrocarbons	B.p., °C/mm	$n^{20}D$	Found %	
			C	H
Hydrocarbon obtained from alcohols	99-100°/1	1.4532	85.62	14.38
n-Nonylcyclohexane	99°/1	1.4530	85.59	14.33

The data presented above show that, under the conditions used, the major products of the oxidation of naphthenic hydrocarbons are alcohols.

The oxidate was saponified with water to decompose the boric acid esters so that the alcohols could be isolated. The unreacted hydrocarbons were separated from the oxygen-containing compounds by chromatography over ASK grade silica gel. Methanol and a petroleum ether boiling up to 60° were used as eluting liquids. Esters were saponified with potassium hydroxide. The alcohols were freed of ketones through the boric acid esters. The bifunctional compounds, which were formed in very small amounts during the oxidation, were separated by chromatography*. The eluting liquids were benzene (at 60°) and methanol (at 20°). The pure alcohols were vacuum distilled. The characteristics of the alcohols obtained are presented in Table 3.

The amounts of the primary and secondary alcohols present in the alcohol fractions were determined [4]. The analytical results are presented in Table 4.

In order to determine whether oxidation of the above-indicated hydrocarbons was accompanied by destruction of the molecules, the alcohols separated from the products of the oxidation of n-nonylcyclohexane were dehydrated over anhydrous aluminum oxide at a temperature of 270°; the reaction was carried out under vacuum. The resulting unsaturated hydrocarbons had an iodine number of 120 (calculated for $C_{15}H_{30}$: 122). These hydrocarbons were hydrogenated in a medium of normal heptane in the presence of Raney nickel catalyst under a hydrogen pressure of 30 atm and at a temperature of 180°; the n-heptane was removed from the hydrogenation products by vacuum distillation. The characteristics of the hydrocarbon obtained from the alcohols are compared in Table 5 with those of the original n-nonylcyclohexane.

*A description of our method for the separation of bifunctional compounds will be published in the near future.

The data of Table 5 show that these hydrocarbons were identical.

Thus, alcohols are formed during the oxidation of naphthenes having side chains of normal structure in the presence of boric acid under the conditions used in the present work. The oxidation proceeds without destruction of the molecules of the substance oxidized. The resulting alcohols are chiefly secondary alcohols having the same number of carbon atoms in the molecule as the original hydrocarbon.

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CIS-TRANS ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF HDROGEN CHLORIDE AND ETHYLUMINUM DICHLORIDE

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We have previously established that organoaluminum compounds and titanium tetrachloride cause isomerization of the cis-units of natural rubber to trans-units [1]. The process of isomerization under the influence of these compounds proceeds at an appreciable rate even at room temperature. The present communication reports the results of an investigation of cis-trans isomerization of natural rubber under the influence of hydrogen chloride and of ethylaluminum dichloride. A number of researches have shed light on the isomerizing effect of hydrogen chloride on unsaturated acids and stilbene [2-7].

Isomerization of a 2% Solution of Natural Rubber in Benzene

Catalyst	Catalyst wt. % of polymer	Temp. °C	Time hours	Structure of chain, %			
				1,4-cis	1,4-trans	3,4	1,2
$Al(C_2H_5)Cl_2$	1,0	30	10	91	8	1	0
The same	1,0	90	10	85	14	1	0
The same	5,0	30	10	75	24	1	0
The same	5,0	90	10	28	65	4	0
HCl (dry)	10,0	80	15	72	26	1	1
The same	50,0	80	15	19	78	1	1
The same	100,0	80	15	0	98	1	1

We investigated the action of dry hydrogen chloride and of ethylaluminum dichloride on benzene solutions of natural rubber under the conditions described previously [1]. The hydrogen chloride was introduced in the form of a saturated solution in benzene. During the investigation of the action of hydrogen chloride, the unsaturation, the chloride content of the polymer chain, and the microstructure were determined for each sample. The microstructures were characterized by means of infrared absorption spectra. As in our previously reported work [1], the quantitative content of cis- and trans-units was determined from the band at 840 cm^{-1}, the intensity and contour of which differ substantially between natural rubber and gutta percha.

In addition, these results were confirmed qualitatively by means of other bands of the spectrum (1100-1150 cm^{-1} and 1300-1330 cm^{-1}).*

* The possibility of using the band at 1300-1330 cm^{-1} was noted in an article recently published by M. A. Golub [9], who investigated the isomerization of natural rubber and gutta percha under the influence of selenium at temperature of 180-200°.

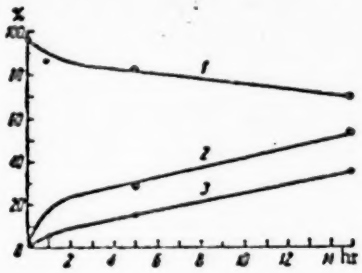

Fig. 1. Degree of isomerization of the polymer and amount of HCl added as functions of the duration of the process at 30° and a weight ratio of HCl to rubber of 1. 1) Content of double bonds in percent of theoretical; 2) amount of trans-units in percent of total double bond content; 3) amount of HCl added in percent of theoretical.

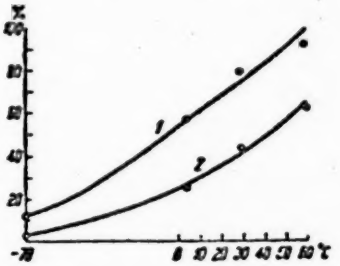

Fig. 2. Effect of temperature on isomerization of the polymer and on the addition of hydrogen chloride (reaction time, 15 hours; weight ratio of HCl to rubber, 1). 1) Amount of trans-units in percent of total double bonds; 2) chlorine content of polymer.

Owing to the partial lowering of the unsaturation of the polymer due to the addition of HCl, the relative content of units in each of the two configurations was calculated in percent of the double bonds remaining in the polymer.

The experimental results are presented in the table and in Figs. 1 and 2. It must be remarked that the data presented on the relative content of cis- and trans-units give only a qualitative picture of the process, since an appreciable decrease in the accuracy of the spectroscopic determinations accompanies the decrease in unsaturation of the polymer. Owing to the limited solubility of the polymer, it was not always possible to compensate for the decrease in double bonds by a corresponding increase in the concentration of the polymer in the solutions investigated. It follows from the data presented in the table that ethylaluminum dichloride and hydrogen chloride have an isomerizing effect on the polymer chain of natural rubber, and the amount of trans-units increases with an increase in the concentration of isomerizing agent.

In both cases, the isomerization process was accompanied by a significant decrease in the unsaturation of the polymer chain. In the case of ethylaluminum dichloride, which is an effective cationic catalyst in polymerization processes, the decrease in unsaturation was apparently connected mainly with an intramolecular cyclization process [8].

In the case of hydrogen chloride, the decrease in unsaturation was associated only with the addition of hydrogen chloride to double bonds, as is illustrated by the data presented in Fig. 1. The amounts of HCl added corresponds to the decrease in chain unsaturation.

With an increase in reaction time, the unsaturation continuously decreased (curve 1), the relative content of trans-units increased (curve 2), and the chlorine content of the polymer continuously increased (curve 3). As Fig. 2 shows, the chain-isomerization and HCl-addition processes began to take place at a temperature of minus 70°, and they were strongly accelerated by an increase in temperature. At a temperature of 60°, the content of double bonds plus the double bonds saturated by addition of hydrogen chloride totaled only 82% of the total double bonds required by theory; this was apparently due to the development of cyclization processes.

The definite correspondence between the cis-trans isomerization processes and the addition of hydrogen chloride is in agreement with the scheme of the process presented earlier [1].

Other experiments carried out by us showed that cis-polybutadiene does not isomerize appreciably under the conditions indicated. The high sensitivity of cis-polyisoprene toward isomerization under the influence of ionic catalysts is probably connected with the branched structure of the units. The fact that stereospecific synthesis of cis-polyisoprene is accomplished considerably more easily than is that of cis-polybutadiene is due to this same cause.

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THE ABSOLUTE CONFIGURATION OF LIGNANS OF THE 2,6-DIPHENYL-3,7-DIOXABICYCLO-[3,3,0]-OCTANE GROUP

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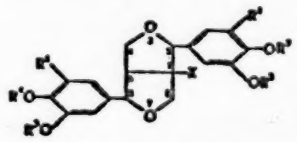
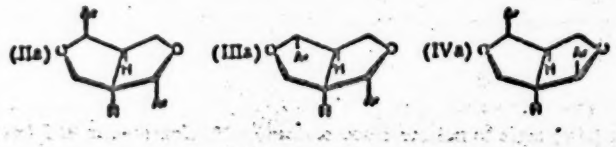
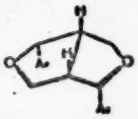
There are currently known 11 natural lignans which are derivatives of 2,6-diphenyl-3,7-dioxabicyclo-[3,3,0]-octane, namely: pinoresinol, (+)-, (−)- and (±)-sesamin, (+)- and (−)-asarinin, eudesmin, symplocosin, phillyrin, liriodendrin, and gmelinol [1-3]. Structural formulas (Ia)-(Ih) have comparatively recently been established for all of these compounds, and many stereochemically important transformations have been studied, but the steric structures (particularly the absolute configurations) have been only partially elucidated. This situation has been brought about by the absence of a critical analysis of the isolated sets of experimental data available in the literature, although, as will be shown below, it is possible rather easily to develop complete steric formulas for the majority of lignans of this group on the basis of the available material.



(Ia) pinoresinol: X = H, $R^1 = R^2 = R^4 = H$, $R^3 = Me$;
(Ib) sesamin: X = H, $R^1 = H$, $R^2 + R^3 = R^3 + R^4 = CH_2$;
(Ic) asarinin: X = H, $R^1 = H$, $R^2 + R^3 = R^3 + R^4 = CH_2$;
(Id) eudesmin: X = H, $R^1 = H$, $R^2 = R^3 = R^4 = Me$;
(Ie) symplocosin: X = H, $R^1 = H$, $R^2 = H$, $R^3 = Me$, $R^4 = \beta$-glucosyl
(If) phillyrin: X = H, $R^1 = H$, $R^2 = R^3 = Me$, $R^4 = \beta$-glucosyl
(Ig) liriodendrin: X = H, $R^1 = R^3 = Me$, $R^2 = R^4 = \beta$-glucosyl
(Ih) gmelinol: X = OH, $R^1 = H$, $R^2 = R^3 = R^4 = Me$.

All of the compounds of this series have cis-attachment of the tetrahydrofuran rings. This follows from the fact that optically active dilactones of dihydroxymethylsuccinic acid (and not the corresponding meso-compounds) are formed during cleavage by nitric acid of the optically active natural lignans and a number of their derivatives [2-6]. It should also be noted that the corresponding trans compounds must be highly strained and, apparently, cannot be formed [7]. Considering this cis-attachment, it is possible for three relative configurations (II), (III), and (IV) of the 2,6-diaryl substituted derivatives under consideration to exist.



(IIb) (IIIb) (IVb) 

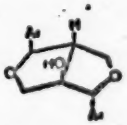
Earlier, in considering the question of the symmetry of certain of these compounds, it was concluded that pinoresinol and sesamin possess an axis of symmetry of the second order, and the aglucon of phillyrin (phillygenol) must be unsymmetrical, as a consequence of which it is necessary to assign to it (and therefore, to the glucoside itself) the relative configuration (II) [2, 5, 6, 8-10]. At the same time a study of the compositions of equilibrium mixtures formed during epimerization of (+)-sesamin and (−)-asarinin [11] led to the conclusion that sesamin has the relative configuration (III) and that asarinin has the configuration (II). The relative configurations of the remaining compounds of this group have not been elucidated up to the present writing.

Since it is known that the methyl ether of phillygenol is the optical antipode of the dimethyl ether of symplocosigenol (the aglucon of symplocosin) [12-14] and that eudesmin is the optical antipode of the dimethyl ether of pinoresinol [8, 13-15], it may be asserted that symplocosigenol and symplocosin have the unsymmetrical structure (II), while eudesmin has a symmetrical structure similar to that of pinoresinol.

Vigorous hydrolysis of the methylenedioxy group of (+)-sesamin and subsequent methylation leads to the formation of a mixture of the dimethyl ether of pinoresinol and the methyl ether of phillygenol [13, 14, 16]. A mixture of eudesmin and the dimethyl ether of symplocosigenol has been obtained by a similar route from (−)-asarinin [13, 14]. Similar mixtures of two isomers are formed during epimerization (under the influence of alcoholic HCl) of the methyl ethers of phillygenol or the dimethyl ethers of pinoresinol and symplocosigenol [9, 14, 16, 17]. The fact that a third pair of isomers was not observed in these mixtures may be considered as evidence of the instability of the latter, which would be expected from compounds of the type of (IV). Consequently, the remaining symmetrical structure (III) must be assigned to pinoresinol and eudesmin.

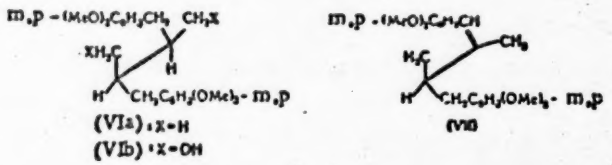
Similarly, in considering the results of the acid hydrolysis of liriodendrin it should be noted that in this case there is obtained a mixture of two aglucons isomeric to the aglucon formed during enzymic hydrolysis (lirioresinol C) [3]; the latter is evidently the unstable isomer. Since data [3] on the molar rotation of the corresponding derivatives show that one of the aglucons formed during acid hydrolysis of liriodendrin (lirioresinol A) corresponds in configuration to phillygenol and the other (lirioresinol B) corresponds to pinoresinol, lirioresinol C and liriodendrin possess configuration (IV).

Data on the configuration of gmelinol are less definite, but a series of assumptions is available. Thus, the probable strain or even the impossibility of the existence of the corresponding trans-attached bicyclic systems and also the almost complete identity of the u.v. spectra of gmelinol and the dimethyl ether of pinoresinol [18] make it reasonable to assume that gmelinol has a cis-configuration of the dioxabicyclooctane nucleus. The fact that during epimerization of gmelinol, the mixture contains only two of the three possible isomers — gmelinol and isogmelinol — [18, 19] makes it possible to assert that gmelinol cannot have an unstable configuration of the type of (IV). Selection between the remaining possible configurations, types (II) and (III), can be made indirectly on the basis that isogmelinol, in contrast to gmelinol, cannot form derivatives at the tertiary hydroxyl [20]. This may be taken as evidence of steric hindrance in the case of isogmelinol; hence structure (Va) or (Vb) may be proposed for gmelinol.

(Va) (Vb) 

The conclusions to be found in the literature and those made by us concerning the relative configurations of natural compounds of the 2,6-diphenyl-3,7-dioxabicyclo-[3,3,0]-octane group may be extended to a consideration of their absolute configurations. It is well known that the (−)-diol (VIb) is formed during catalytic hydrogenation of the dimethyl ether of pinoresinol in the presence of Pd and that this diol can be converted to the dimethyl ether of (−)-dihydroguaiaretic acid (VIa) [21]. Consequently, the two asymmetric centers of the latter correspond to centers 1 and 5 in pinoresinol. The absolute configuration of ether (VIa) can be deduced on the basis

of the fact that it is formed (together with the corresponding meso-compound) upon reduction of the ether of (−)-guaiaretic acid (VII) [22], the configuration of the only asymmetric atom of which was recently established [23]. Knowing the relative configuration of all of the centers of pinoresinol, formula (IIIa) may be selected as representing its absolute configuration, and pinoresinol may be described in conventional symbols [24] as (1R, 2S, 5R, 6S)-2,6-diaryl-3,7-dioxabicyclo-[3,3,0]-octane. (+)-Sesamin also has this same configuration (IIIa), but (−)-sesamin and eudesmin (the optical antipode of the dimethyl ether of pinoresinol) must have the antipodal (1S, 2R, 5S,6R) configuration (IIIb).



(VIa) X=H
(VIb) X=OH

(VII)

(+)-Asarinin differs from (+)-sesamin configuration only at one center, C_2; therefore, its absolute configuration, as well as the configuration of phillyrin, can be described as (1R, 2R, 5R, 6S) and represented by formula (IIa). In conformity with this, (−)-asarinin and symplocosin must have the (1S, 2S, 5S, 6R) configuration (IIb). Since the configuration of the C_1 and C_5 atoms of liriodendrin must be the same as in pinoresinol, the (1R, 2R, 5R, 6R) configuration represented by formula (IVa) can be assigned to it. Finally, we feel that the (1S, 2S,5R, 6R) configuration (Va) may be proposed for gmelinol. This proposal is based on the fact that gmelinol, isogmelinol, and a number of their derivatives are dextrorotatory [18, 20]. The lignans described above and their derivatives, which have structures (IIa) and (IIIa), are also dextrorotatory, which suggests that the 1 and 5 centers of gmelinol have a similar configuration; hence, formula (Va) can be assigned to gmelinol. Actually, this proposal is not in good agreement with data on the shift of the optical rotation of certain derivatives of gmelinol and isogmelinol [18].

On the basis of our analysis of the experimental data, it may be considered that the absolute configurations of pinoresinol, (+)- and (−)-asarinins, (+)- and (−)-sesamins, eudesmin, and symplocosigenol have been demonstrated. The absolute configuration of liriodendrin can be assumed with a high degree of reliability. Since in the case of gmelinol the relative configuration has not been strictly proved, our proposed absolute configuration is conjectural to some extent. Finally, the absolute configurations of phillyrin and symplocosin can be described only in general forms — by formulas (IIa) and (IIb), respectively — since these lignans have nonequivalent aryl radicals, the positions of which have not been established. However, the case of symplocosin is somewhat simplified by the fact that the aryl radicals of its aglucon are equivalent, and consequently, the absolute configuration of the latter is proved.

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EQUILIBRIUM DIAGRAM OF THE TERNARY SYSTEM Ti–Al–Sn

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Alumin and tin are important components of titanium alloys. Certain alloy compositions distinguished by high thermal stability have been developed on the basis of alpha solid solutions in the ternary system Ti–Al–Sn [1]. Hower, we were unable to find in the literature any data regarding the equilibrium diagram of the ternary system Ti–Al–Sn.

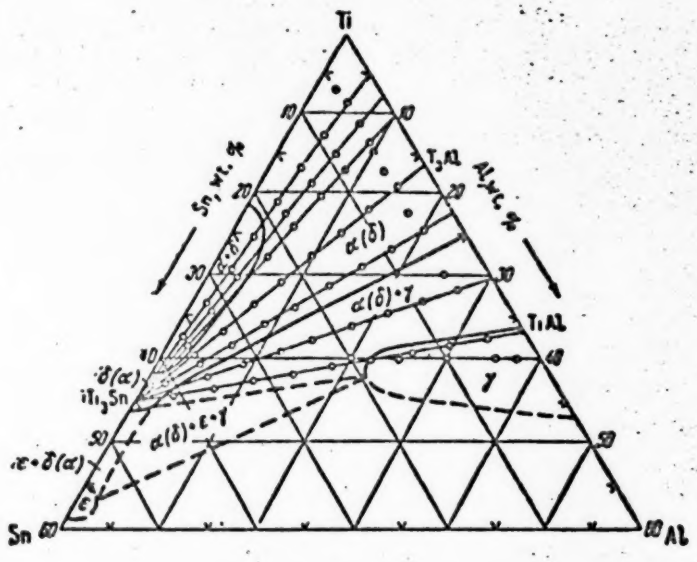

Fig. 1. Titanium–aluminum–tin phase diagram at 600°.

The aim of the present work was the study of the equilibrium of alloys of the ternary system Ti–Al–Sn in the region bounded by the partial ternary system Ti–Ti_3Sn–TiAl. Consideration of the binary systems composing this ternary system (Ti–Al and Ti–Sn) shows that limited solid solutions based on α-titanium are formed in these systems by a peritectoid reaction between the β-phase of titanium and the γ-phase (which is based on the compound TiAl) at 1240° in the Ti–Al system and between the β-phase of titanium and the δ-phase (which is based on the compound Ti_3Sn) at 890° in the system Ti–Sn, respectively.

Fig. 2. Microstructures of alloys, 200 x: a) 18% Sn, 10% Al: α(δ)-phase; b) 27% Sn, 2.5% Al: (α + δ)-phase.

There have recently appeared in the literature a series of papers reporting studies of the equilibrium diagram of the system Ti–Al [2-5]; these papers reported data concerning the possible existence of new compounds (Ti_3Al and $TiAl$) in the region of alpha solid solution, which, according to reference [6], was orginally considered to extend to a concentration of about 25% Al. In conformity with the available literature data [3,4] it may be assumed that in the system Ti–Al there exists an ordered Ti_3Al phase, which probably has a large region of homogeneity (12-25% Al) with the same distribution of atoms as in the ordered Ti_3Sn phase in the system Ti–Sn [7]. Microstructural and x-ray methods of investigation were used in the present work, and the hardness of the alloys was also studied. The alloys were prepared by fusion in an arc furnace with an unconsumable electrode. Titanium produced by the iodide method and by reduction at high temperature with magnesium (TG-00 grade) was used; 99.99% pure aluminum and 99.9% pure tin were used. Since equilibrium is reached very slowly in the system Ti–Al–Sn when undeformed samples are used, all of the alloys (with the exception of alloys of cast sections Ti_3Sn–TiAl and through 30% Al) were forged. In this manner, our aim of accelerating the process of obtaining the alloys in the equilibrium state was achieved.

The alloys were subjected to the following stepwise heat treatment under vacuum: homogenization at 1200° for 100 hours and annealing at 1100° for 50 hours, 1000° for 200 hours, 800° for 300 hours, 600° for 500 hours and subsequent cooling in the furnace. Alloys of the section Ti_3Sn–TiAl were annealed for a longer time in accordance with the regime: 1000° for 500 hours, 800° for 1000 hours, 600° for 1200 hours, and subsequent slow cooling to room temperature. The majority of the cast alloys studied were found to have a lamellar or needle structure of the alpha phase. The phase diagram of that part of the Ti–Al–Sn system studied was constructed for a temperature of 600° using the data from the microstructural and x-ray investigations (Fig. 1).

As a result of these investigations, the presence in the Ti–Al–Sn system of the following phases has been established:

1) a solid solution of aluminum and tin in α-titanium (α);

2) a solid solution based on the chemical compound TiAl (γ);

3) continuous solid solutions of the compounds Ti_3Al and Ti_3Sn, which correspond in structure to α- or δ-phases;

4) a solid solution based on the chemical compound Ti_3Sn(δ).

That part of the Ti–Al–Sn phase diagram studied, which corresponds to an isothermal section at 600° for annealed alloys, is presented in Fig. 1. As may be seen from Fig. 1, the major part of the diagram is occupied by the single-phase region of the ternary α(δ)-solid solution based on titanium and the quasibinary section Ti_3Al–Ti_3Sn. One fact which merits attention is that in the annealed samples all alloys of the sections Ti_3Al–Ti_3Sn and through 22% Al have a single-phase solid solution with a polyhedral structure (Fig. 2,a), which confirms the existence of continuous solid solutions between these two compounds. The x-ray patterns of annealed alloys of these sections were identical for all of the alloys studied, and they did not have any lines other than those characteristic of α- or δ-phases. The formation in the annealed samples of continuous solid solutions between the δ-phase (based on Ti_3Sn) and the homogeneous α-phase of the system Ti–Al can most probably be explained by the possible presence in this system of an ordered Ti_3Al phase isomorphic with Ti_3Sn. The chemical behavior of these compounds of aluminum and tin with titanium have much in common. The compounds Ti_3Al and Ti_3Sn have isomorphic crystal structures, and, apparently, the same type of chemical bond is involved; consequently, all of the conditions required for the formation of continuous solid solutions between the compounds Ti_3Al and Ti_3Sn are met.

A consideration of the equilibrium diagram of the Ti–Al–Sn system at 600° shows that the α(δ)-solid solutions occupy a large region of the concentration triangle (see Fig. 1).

In view of the possible formation of continuous solid solutions between α-titanium and Ti_3Sn [8], alloys having a two-phase structure, α + δ (Fig. 2,b), were subjected to additional annealing at 800° for 1000 hours. This thermal treatment led to a certain change in the microstructure of these alloys. Thus, under the given conditions for attaining the equilibrium state (annealing regime indicated above), the presence in the equilibrium diagram of a two-phase system, α + δ, lying toward the Ti–Sn side is characteristic (Fig. 1).

The boundaries of the gamma region (based on the compound TiAl) in the ternary system Ti–Al–Sn were also established by means of the microstructural and x-ray phase investigations. As may be seen from the diagram, the region of the γ-solid solution extends over a considerable portion of the diagram (up to about 18% Sn). The remaining part of the equilibrium diagram is occupied by the two-phase region α + δ.

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COEXTRACTION OF TUNGSTEN AND CERTAIN OTHER ELEMENTS

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While the phenomena of coprecipitation and cocrystallization have undergone considerable investigation, little study has been made of coextraction of elements. Only isolated facts relating to this phenomenon are known.

TABLE 1

Effect of Dilution on the Extraction of Tungsten and Molybdenum by Aniline (pH of the aqueous phase after extraction 4.3-4.5)

Concentration of elements γ/ml	Distribution coefficient	
	W^{VI}	Mo^{VI}
10,000	4900	420
1000	800	42
100	140	5.4
10	30	1.5
1	9	–

Owing to the absence of a solid phase, adsorption does not occur during extraction, though adsorption does lie at the foundation on which many instances of coprecipitation and cocrystallization rest. In the case of extraction, processes similar to adsorption can proceed only at the interface between the phases; however, such processes proceed only to a slight extent.

Coextraction takes place by a different mechanism; probably the most important difference is the formation of mixed compounds.

Coextraction is sometimes associated with conversion of the element to a compound which is more readily extracted than is the original compound. It is a known fact that coextraction of pentavalent vanadium with tungsten and phosphorus is a consequence of the readily extractable mixed phosphotungstomolybdic heteropoly acid [1]. The ease with which this compound is formed permits its use for the colorimetric determination of small amounts of vanadium [2].

In a number of other cases, described in the literature, in which there is a substantial increase in the extraction of elements in the nonaqueous solvent, the formation of new, readily extractable compounds is less evident. The increase in the extractability of ruthenium by a benzene solution of butyric acid after the addition of copper [3] or by methyl isopropyl ketone after the introduction of lead [4] may be cited as examples. Other cases of coextraction in which the mechanism is not clear have also been described [5-7].

A clear-cut example of coextraction by a mechanism involving formation of mixed compounds has been observed by the authors during an investigation of tungsten and molybdenum extraction from a HCl medium by aniline. In this case, the tungsten and molybdenum were extracted by the so-called onium mechanism [8] in the form of aniline polytungstates or polymolybdates, the anions of which were formed during acidification of the

TABLE 2

Effect of the Presence of Molybdenum and Vanadium on the Distribution Coefficients of Tungsten (the values shown are averages of two determinations)

Concentration of W^{VI}, γ/ml	W distribution coefficients				
	without addition	with Mo^{VI}		with V^{V}	
		500 γ/ml	250 γ/ml	500 γ/ml	250 γ/ml
1.0	9.0	4450	38	4670	29
0.1	5.0	1600	–	1700	–
0.01	2.5	250	–	295	–
0.001	1.3	18	–	40	–

TABLE 3

Coextraction of Niobium with Tungsten and Vanadium at 20°

Nb concentration, γ/ml	Nb distribution coefficients		
	without addition	with addition of 500 γ/ml	
		W	V^{V}
1.0	5.2	330	37
	5.0	240	35
0.01	0.45	280	25
	0.67	250	–
	0.87	–	–

soluble tungstates and molybdates. When, after acidification of the tungstate and molybdate solutions, dilution of these elements is sufficiently high, the required polyanions are not formed, and, therefore, the extraction of either tungsten or molybdenum from dilute solutions is less effective than from more concentrated solutions. After acidification of an aqueous solution of sodium tungstate or molybdate with hydrochloric acid to an acidity of 1.5 N and agitation with an equal volume of aniline, the tungsten or molybdenum passes into the aniline layer, the distribution coefficient rapidly decreasing with a decrease in the concentration of the tungsten or molybdenum (Table 1). But, if to a dilute solution of an alkali metal tungstate is added not too small an amount of a molybdate or vanadate and the entire mixture is then acidified with hydrochloric acid to the same acidity (1.5 N), the distribution coefficients of the tungsten are substantially increased. The results of experiments carried out with W^{185} or W^{187} are presented in Table 2.*

It is evident that tungstates form mixed polyanions with molybdates or vanadates and that the tungsten is extracted in the form of these mixed polyanions. The tendency of these elements to form mixed compounds is evident from the existence of well-known mixed heteropoly acids [9].

Coextraction of this type is possible not only with tungsten, but also with other elements which have a tendency to form oxy-oxo ions, sometimes called "polymers" in the literature. Thus, niobium can be coextracted with tungsten and also with vanadium. During extraction with aniline, the distribution coefficients of niobium are small when the niobium concentration is low, and they also decrease with a decrease in niobium concentration. But, if a coextraction element is introduced into the alkaline niobate solution and the entire mixture is

* Experiments with a tungsten concentration of 1.0 γ/ml and higher were carried out with W^{185}, while experiments with lower concentrations were carried out with W^{187}.

TABLE 4

Extraction of W and Mo with Aromatic Amines from 0.05 N Solutions of Na Tungstate and Molybdate Acidified with HCl to an Acidity of 0.5 N

Amine	Distribution coefficient	
	W	Mo
Aniline	1500	90
m-Toluidine	1050	130
p-Xylidine	1000	300
m-Xylidine	875	240
α-Naphthylamine	625	225

then acidified, the distribution coefficients increase sharply. Table 3 presents the results of comparative experiments. An alkaline solution of sodium tungstate or vandate was added to an alkaline solution of potassium niobate with Nb^{95}, carrier-free grade, and the mixture was carefully agitated, acidified with hydrochloric acid to an acidity of 1.5 N and then extracted with an equal volume of aniline.

The cases of coextraction which have been considered here in detail can be of interest: 1) for the purpose of concentrating the respective elements from dilute solutions during analytical determinations, since the extraction can be quite selective; 2) for investigating the ability of elements to form mixed polynuclear oxy-oxo ions and other mixed molecules which have not been sufficiently studied.

We should emphasize that in carrying out experiments like those described, it is expedient to use substances which, like aniline, form cations with an average, not too large ionic weight. If amines or other cation-forming compounds with too high a molecular weight are used (methyl violet, for example) then, owing to their ability to extract "inonomeric" tungstate ions, cases of coextraction like those considered are less clearly observed.

The inability of aniline to extract tungsten in the form of the normal aniline tungstate is shown by the lack of extraction of tungsten during extraction of unacidified sodium tungstate solutions. The possibility that the absence of extraction from unacidified solutions could be due to an insufficient concentration of anilinium cations under these conditions is negated by the results of experiments with benzylamine as the extractant.

The molecular weight of benzylamine, $C_6H_5CH_2NH_2$ (mol. wt. 107) does not differ greatly from that of aniline, $C_6H_5NH_2$ (mol. wt. 93), but it is more strongly basic than aniline. The dissociation constants for aniline and benzylamine at 25° are, respectively, $4.0 \cdot 10^{-10}$ and $2.4 \cdot 10^{-5}$; benzylamine is miscible with water. It is easily calculated that, for example, in a 50% solution of benzylamine in a medium with a pH of 9.5 the concentration of benzylamine cations will be of the order of 3.5 moles/liter, as compared to a tungsten concentration of $3 \cdot 10^{-3}$ mole/liter. Nevertheless, neither benzylamine containing 10% dibenzylamine nor its 1:1 mixture with aniline extracts tungsten from unacidified solutions of sodium tungstate with a pH of 9.5 (after extraction). At a tungsten concentration of 1 mg/ml, the distribution coefficient of tungsten is less than 0.01 in both cases.

Extraction and coextraction of tungsten and molybdenum does not occur only with aniline. Benzylamine and its mixture with dibenzylamine are not suitable for this purpose, since an amine phase cannot exist in equilibrium with a medium with a pH of 4.2-4.5. Amines with less basic properties – meta-toluene $K^{25} = 5.5 \cdot 10^{-10}$), p-xylidine ($K^{25} = 9.6 \cdot 10^{-10}$), m-xylidine ($K^{25} = 6.3 \cdot 10^{-10}$), dilute α-naphthylamine (m.p. 50°, $K = 9.9 \cdot 10^{-11}$) and the like – extract tungsten or molybdenum just as aniline does (Table 4).

The cases of coextraction of tungsten and niobium which have been considered here are of practical interest, since they indicate the possibility of increasing the extractability of these elements from dilute solutions, and since they can no doubt be extended to a number of other elements. Many elements are capable of forming polynuclear oxy-oxo ions, and many elements can be coextracted if the experiment is appropriately designed. All such cases of coextraction proceed by a mechanism involving the formation of mixed compounds.

The literature contains references to cases of relatively small increases in the extractability of certain elements when large amounts of other readily extractable elements are introduced into the solutions. Thus, it has been noted that Cs, Ca, Sr, and La, for example, are less readily extracted by methyl butyl ketone from solutions which do not contain uranyl nitrate than from solutions containing uranyl nitrate, which is very readily extractable [5].

It is difficult to say whether the increase in extractability of these elements upon the addition of uranyl nitrate is a consequence of true coextraction or whether it is due to other causes.

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SYNTHESIS AND SOME CONVERSIONS OF ALKYLMERCAPTODIBORANES

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(Presented by Academician B. A. Kazanskii, December 22, 1959)

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In a letter to the editor of another publication [1], we reported on the reaction between diborane and mercaptans. We have now investigated the reaction between diborane and n-propyl mercaptan and n-butyl mercaptan in ether solution at room temperature and with different reactant ratios.

When an excess of the mercaptan is used, the major reaction product is a tetraalkylmercaptodiborane:

$$B_2H_6 + 4RSH \rightarrow (RS)_2\,BHBH\,(SR)_2 + 4H_2.$$

$$R = n\text{-}C_3H_7,\quad n\text{-}C_4H_9.$$

These compounds are distinguished by their considerable stability. They remain unchanged during prolonged storage, and they can be distilled under vacuum. It is interesting that the tetraalkylmercaptodiboranes distill in the form of extremely viscous liquids which again become mobile after a few hours. Cryoscopic determination of the molecular weight gives a value approximately two-thirds that of the molecular weight of the dimeric form of the dialkylmercaptoborane. It is evident that our alkylmercapto derivatives of diborane undergo partial dissociation in benzene solution. When the reaction between diborane and n-butyl mercaptan is carried out at a mole ratio of diborane to mercaptan of 1 : 2, significantly less tetra-n-butylmercaptodiborane is obtained, and the major product is di-n-butylmercaptodiborane, $C_4H_9SBH_2BH_2SC_4H_9$. This compound is unstable, and even on standing at room temperature it symmetrizes to diborane and tetra-n-butylmercaptan. In identifying the di-n-butylmercaptodiborane, we made use of its ability to react with olefins at room temperature with the formation of n-butyl esters of dialkylborinic acids:

$$[(C_4H_9S)\,BH_2]_2 + 4CH_2{=}CHR \rightarrow 2C_4H_9SB\,(CH_2CH_2R)_2.$$

By passing propylene into the reaction mixture obtained from the interaction of diborane and n-butylmercaptan (reactant ratio of 1 : 2) we obtained: tri-n-propylboron (8%), which was formed from the unreacted diborane; the n-butyl ester of di-n-propylthioborinic acid (40%); and tetra-n-butylmercaptodiborane (24%), which does not react with propylene under the conditions used. When propylene was passed into a reaction mixture which had been allowed to stand overnight, more tri-n-propylboron (18%) and tetra-n-butylmercaptodiborane (37%) were obtained, while the amount of n-butyl ester of di-n-propylthioborinic acid formed was very small (5%).

It was also found to be possible to prepare di-n-butylmercaptodiborane by the action of diborane on tetra-n-butylmercaptodiborane; however, the yield was very small, since an equilibrium, which may be expressed by the equation below, is established between the initial reactants and the reaction products:

$$(C_4H_9S)_2\,BHBH\,(SC_4H_9)_2 + B_2H_6 \rightleftarrows 2C_4H_9SBH_2BH_2SC_4H_9.$$

It should be remarked that Burg and Wagner [2] obtained a polymer of the composition $(CH_3SBH_2)_x$ by the vapor phase reaction between diborane and methyl mercaptan. Tetraalkylmercaptodiboranes have very interesting chemical properties. The hydrogen atoms in these compounds are significantly less reactive than those in diborane. This is indicated primarily by the fact that the trialkyl thioborate is not formed under conditions under which these compounds are synthesized in the presence of a large excess of mercaptan. The reaction of a tetraalkylmercaptodiborane with a mercaptan begins at 50-60°, and proceeds vigorously at the boiling point of the mercaptan. The reaction yields the trialkylthioborate:

$$[(RS)_2BH]_2 + 2\,RSH \rightarrow 2\,(RS)_3B + 2H_2,\ R = n\text{-}C_4H_9,\ n\text{-}C_4H_9.$$

Hydrogen is not evolved when tetra-n-butylmercaptodiborane is treated with alcohol at room temperature. N-trialkylborazoles were obtained by the action of primary amines (ethylamine, n-butylamine) on tetra-n-butylmercaptodiborane under the same conditions.

Apparently, a complex (I) of the corresponding dialkylmercaptoborane with the amine is formed in the first stage of the process, and this is converted into an alkylmercaptoalkylaminoborane (II) by the elimination of a molecule of mercaptan. Mercaptan is then eliminated from the latter with the formation of the N-alkylborazole:

$$[(C_4H_9S)_2BH]_2 + 2RNH_2 \rightarrow 2\,(C_4H_9S)_2BH\cdot NH_2R.$$
(I)

$$(C_4H_9S)_2BH\cdot NH_2R \rightarrow \begin{matrix} C_4H_9S \\ \diagdown \\ BH \\ \diagup \\ RNH \end{matrix} + C_4H_9SH.$$
(II)

$$3\begin{matrix} C_4H_9S \\ \diagdown \\ BH \\ \diagup \\ RNH \end{matrix} \rightarrow \begin{matrix} & & BH & & \\ & \diagup & & \diagdown & \\ RN & & & & RH \\ | & & & & | \\ BH & & & & BH \\ & \diagdown & & \diagup & \\ & & NR & & \end{matrix} + 3C_4H_9SH,\quad R = C_2H_5,\ n\text{-}C_4H_9.$$

The high strength of the B—H bond in tetraalkylmercaptodiboranes appears in reactions with olefins. We were unable to carry out the addition of tetra-n-butylmercaptodiborane to olefinic hydrocarbons by heating the reactants at 70° in the presence of pyridine.

EXPERIMENTAL

All operations with organoboron compounds were carried out in an atmosphere of nitrogen. Diborane was synthesized in 80-85% yield from boron trifluoride etherate and lithium aluminum hydride [3].

1. Tetra-n-butylmercaptodiborane. A solution of 40.5 g (0.45 mole) of n-butyl mercaptan in 50 ml of absolute ether was charged to a three-neck flask fitted with a stirrer with mercury seal, a gas inlet tube, and a reflux condenser. Diborane was passed into the reaction mixture at room temperature for two hours, whereupon heat was evolved, and the mixture became viscous. On the following day, the ether was evaporated under water-aspirator vacuum, and the residue was distilled. This yielded 15.7 g of tetra-n-butylmercaptodiborane with b.p. of 98-103° at 2 mm. The yield was 75%. After an additional distillation, the material had a b.p. of 89-90° at 1 mm, d^{20}_4 0.9561; n^{20}_D 1.5170.

Found %: C 50.58, 50.45; H 10.30, 10.38; B 5.81, 5.54 $C_{16}H_{38}B_2S_4$. Calculated %: C 50.52; H 10.07; B 5.68

Molecular weight 256 and 258 *; calculated. 380.

During distillation of the tetra-n-butylmercaptodiborane, 2.1 g of a liquid (boron content 9.29%) was collected in a trap cooled to −70°; this material was probably a mixture of boron hydrides having a low degree of substitution.

* The molecular weight was determined cryoscopically in benzene.

2. Tetra-n-propylmercaptodiborane. In a similar manner, from 34.3 g (0.45 mole) of n-propyl mercaptan and 0.55 mole of diborane was obtained 10.0 g (56%) of tetra-n-propylmercaptodiborane, b.p. 93-95° at 4 mm, d^{20}_4 0.9809; n^{20}_D 1.5265.

Found %: C 44.37; 44.67; H 9.52; 9.54; B 6.24, 6.50 $C_{12}H_{28}B_2S_4$. Calculated %: C 44.45; H 9.33; B 6.67

Molecular weight: found, 239, 237; calculated, 324.

3. Interaction of Diborane and n-Butyl Mercaptan at a Ratio of 1 : 2. The experiment was carried out similarly to the preparation of tetra-n-butylmercaptodiborane. A total of 0.07 mole of diborane was passed, over a period of four hours, into a solution of 12.6 g (0.14 mole) of n-butyl mercaptan in 75 ml of absolute ether. After the unreacted gaseous diborane has been purged from the flask with nitrogen, a slow stream of propylene was passed into the reaction mixture for two hours. The reaction with propylene was exothermic. The ether was distilled under water-aspirator vacuum, and the residue was subjected to fractional distillation. The following fractions were obtained: 1) 48-50° at 11 mm, 1.5 g; 2) 64-70° at 2 mm, 10.4 g; 3) 98-105° at 2 mm, 6.4 g. During distillation of the latter fraction, 0.6 g of material (boron content, 10.11%) was collected in a trap cooled to −70°.

The first fraction was tri-n-propylboron. The yield was 7.9%, calculated on the diborane taken for the reaction; $n^{20}D$ 1.4100 (literature b.p. 62°/20 mm, $n^{22.6}D$ 1.4135 [4]). The second fraction was the n-butyl ester of di-n-propylthioborinic acid; the yield was 0.056 mole (40%), $n^{20}D$ 1.4563 (literature b.p. 98°/11 mm, $n^{20}D$ 1.4598 [5]). The third fraction was tetra-n-butylmercaptodiborane; the yield was 0.017 mole (24%) $n^{20}D$ 1.5150.

4. Interaction of Diborane and Tetra-n-butylmercaptodiborane. A solution of 10.1 g (0.053 mole) of tetra-n-butylmercaptodiborane in 30 ml of ether was charged to a two-neck flask fitted with a gas inlet tube and reflux condenser, and the solution was saturated with diborane over a two-hour period. On the following day, propylene was passed into the solution for two hours, until the evolution of heat ceased. The solvent was distilled under water-aspirator vacuum, and the residue was fractionated. There was obtained 2.8 g (0.020 mole) of tri-n-propylboron, b.p. 48-53°/13 mm, $n^{20}D$ 1.4195; 2.4 g (0.013 mole) of the n-butyl ester of di-n-propylthioborinic acid, b.p. 65-70°/2 mm, $n^{20}D$ 1.4570; and 5.7 g (0.030 mole) of tetra-n-butylmercaptodiborane, b.p. 105-110°/3 mm, $n^{20}D$ 1.5140.

During distillation of the latter fraction, 1.6 g of a material containing 10.89% boron condensed in a trap cooled to −70°.

5. Tri-n-butyl Thioborate. A mixture of 7.4 g (0.020 mole) of tetra-n-bucylmercaptodiborane and 4.2 g (0.046 mole) of n-butyl mercaptan was charged to a two-neck flask fitted with a thermometer and a reflux condenser, the end of which was connected to a gas meter, and the mixture was heated for four hours. Evolution of gas began at 60°; toward the end of the reaction, the temperature of the reaction mixture increased to 150°. A total of 870 ml of hydrogen was obtained during the experiment.

The liquid reaction products were vacuum distilled. There was obtained 7.9 g (70%) of tri-n-butyl thioborate; b.p. 150-152° at 1 mm; d^{20}_4 0.9684; $n^{20}D$ 1.5205.

Found %: C 51.89, 52.05; H 10.03, 9.78; B 3.88; 3.87 $C_{12}H_{27}BS_3$. Calculated %: C 51.77; H 9.79; B 3.89

6. Tri-n-propyl Thioborate. Similarly, from 5.3 g (0.016 mole) of tetra-n-propylmercaptodiborane and 5.0 g (0.066 mole) of n-propyl mercaptan was obtained 6.1 g (78%) of tri-n-propyl thioborate, b.p. 135-135.5°/4 mm, d^{20}_4 0.9952; $n^{20}D$ 1.5312.

Found %: C 46.01, 45.76; H 8.90, 8.76; B 4.62, 4.66 $C_9H_{21}BS_3$. Calculated %: C 45.75; H 8.98; B 4.58

7. Triethylborazole. To 16.5 g (0.43 mole) of tetra-n-butylmercaptodiborane in a two-neck flask fitted with a dropping funnel and reflux condenser was added 4.8 g (0.107 mole) of ethylamine. The addition of the ethylamine was accompanied by evolution of heat. The reaction mixture was allowed to stand for an hour at room temperature, and the mercaptan was then distilled under water-aspirator vacuum; heating of the mixture was initially at 30-40°, and this was increased to 90-100° toward the end. The mercaptan evolved (18 ml) was condensed in a receiver cooled to −70°. The residue was twice distilled under vacuum. There was obtained 3.7 g of N-triethylborazole, b.p. 66-68° at 20 mm, $n^{20}D$ 1.4373 (literature: $n^{20}D$ 1.4344 [6]). The yield was 77% of theoretical.

8. N-tri-n-butylborazole. The reaction between 11.6 g (0.03 mole) of tetra-n-butylmercaptodiborane and 4.4 g (0.06 mole) of n-butylamine was carried out in a manner similar to the preceding experiment. After removal of the mercaptan, 3.3 g (66%) of N-tri-n-butylborazole was obtained from the residue; b.p. 78-80° at 0.25 mm; d^{20}_4 0.8426; $n^{20}D$ 1.4515.

Found %: C 57.41, 57.51; H 12.26, 12.22; B 13.52, 13.45 $C_{12}H_{30}N_3B_3$. Calculated %: C 57.91, H 12.15; B 13.04

In addition, 1.0 g of a crystalline material was obtained; this was not investigated in detail.

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IODONIUM DERIVATIVES OF 5-PHENYL-1,3-CYCLOHEXANEDIONE AND THEIR TRANSFOMATIONS

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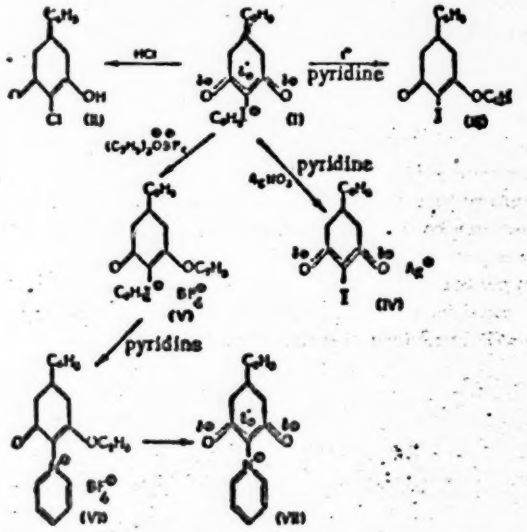
During an investigation of the reactions of β-diketones with phenyliodoso compounds it was found that 5-phenyl-1,3-cyclohexanedione reacts similarly to dimedone [1], forming a new compound, the internal iodonium salt (I) which can be regarded as formed, analogously to a betaine, by intramolecular change from the phenyl ether of the monoenol form of 2-iodo-5-phenyl-1,3-cyclohexanedione (III).* In further reference to this compound, we shall call it phenyliodone. This communication reports the results of a study of the properties and structural features of phenyliodone and of its alkylation and cleavage products.

Phenyliodone is a white substance which dissolves in chloroform and benzene, imparting to the solution an intense yellow color. The substance is not very stable, and it undergoes cleavage under the action of various reagents. Phenylindone is particularly sensitive to the action of sunlight. Cleavage can be carried out with rupture of the iodine—carbon bond in two directions, as is typical of unsymmetrical iodonium compounds. Thus, in the presence of hydrochloric acid, phenyliodone is smoothly cleaved to iodobenzene and 2-chloro-5-phenyl-1,3-cyclohexanedione (II), while both iodobenzene and the phenyl ether of the enol form of 2-iodo-5-phenyl-1,3-cyclohexanedione (III) are formed as cleavage products in pyridine solution under the influence of temperature. Cleavage occurs only at the iodine — phenyl bond in the presence of silver nitrate and pyridine, and the silver salt of 2-iodo-5-phenyl-1,3-cyclohexanedione (IV) is formed.



(II) (I) (III) (V) (IV) (VI) (VII)

* The name given to (I) in the original is "enolatebetainephenyl-(5-phenyl-1,3-cyclohexanedion-2-yl)iodonium". The nomenclature in the remainder of the translation is generally based on that of the original authors.—Publisher.

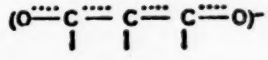
Phenyliodone is not cleaved by strong acylating and alkylating agents (benzoyl chloride, triethyloxonium fluoborate); instead, acyl or alkyl derivatives are formed. The interaction of triethyloxonium fluoborate and phenyliodone yields phenyl-(O-ethyl-5-phenyl-1,3-cyclohexanedion-2-yl)iodonium fluoborate (V), a white substance of low stability. In the presence of pyridine, this iodonium salt readily undergoes cleavage to iodobenzene and N-(O-ethyl-5-phenyl-1,3-cyclohexanedion-2-yl)pyridium fluoborate (VI). The latter compound saponifies readily to form the corresponding pyridinium betaine of the enol form (VII).

Thus, there is an interesting directional rupture of the iodine – carbon bonds in the iodonium derivatives investigated which depends on structural peculiarities and the reagent; this property has already been noted in the analogous dimedone derivatives [2]. Since it is assumed that in iodonium compounds, the bond with the lowest electron density is ruptured [3], it naturally follows that in nonacidic media, the iodine–phenyl bond in phenyliodone is characterized by a lower electron density than the bond between iodine and the β-diketone radical. This is clearly apparent from the study of the cleavage of phenyliodone in the presence of silver nitrate and pyridine. Under these conditions, phenyliodone undoubtedly exists in the enolate form, from which it follows that the electron density at the carbon atom of the active methylene group of the enolate anion form is higher than it is at this same carbon in the un-ionized form. For example, in the presence of hydrochloric acid, phenyliodone exists in the un-ionized form, and cleavage occurs at the bond between the iodine and the β-diketone residue. This same thing is also true of cleavage of alkyl derivatives of phenyliodone. Consequently, the enolate anion system is characterized by a high mobility of electronic charge.

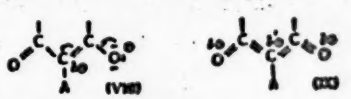
Curious conclusions may be drawn from a study of the absorption spectra of phenyliodone (I) and the pyridinium betaine of enol form (VII). The normal enolate anion system of 5-phenyl-1,3-cyclohexanedione (for example, in the sodium salt) is characterized in the infrared region by a very intense absorption at 1510-1530 cm^{-1}. In the ultraviolet spectra there is a maximum at about 282 mμ, which is characteristic of 1,3-cyclohexanedione enolate anions. The iodine atom causes a significant decrease in the frequency of the enolate anion system, since the silver salt of 2-iodo-5-phenyl-1,3-cyclohexanedione (IV) absorbs strongly in the region of 1470-1490 cm^{-1}.

However, in chloroform solution, phenyliodone absorbs strongly at 1564 cm^{-1}, and the pyridinium betaine of enol form absorbs at 1546 cm^{-1}. In methanol solution, the absorption maximum in the ultraviolet region is found at 261 mμ for phenyliodone and at 252 mμ for the pyridinium betaine of enol form (VII). This phenomenon has also been observed with the analogous dimedone derivatives [4].

In the spectra of enolate anion systems of the betaines of enol form, such a large shift in the characteristic maximums away from the maximums of the normal system can be explained only by a change in the electronic structure and in the nature of the multiple bonds. It is natural to assume that under the influence of a positively charged substituent, the electron density at the carbon atom of the active methylene group is increased, and by the same token there is a change in the character of the carbon-carbon and carbon-oxygen bonds of the system



There presently exists no satisfactory method for reflecting the correct structure of enolate anions. The complete equality of the charges on the two oxygen atoms is well represented by the dotted line symbolism of partial bonds [5] [for example, in (IV)], which is the current practice. It is only necessary to keep in mind the equality of the two carbonyl groups in symmetrical systems. But it is a fact that, as shown by our examples, under the influence of various structural factors the electron density at the carbon and oxygen atoms can change, and the fractional charges localized at the individual atoms is still difficult to evaluate. By the same token, it is naturally difficult to represent correctly the structure of betaines of enol form. The extant method (VIII) is not sufficiently accurate.



Method (IX), which was used in our recent articles, would appear more correct, considering that the fractional charges δ and δ' are still difficult to evaluate, but $2\delta + \delta' = 1$.

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PREPARATION OF THE HEXACYCLIC PRODUCT OF THE AUTOCONDENSATION OF CYCLOHEXANONE

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We have recently shown [1] that autocondensation of cyclohexanone under the influence of solid sodium hydroxide at room temperature leads to the formation of a tricyclic dihydroxy ketone, $C_{18}H_{30}O_2$. The condensation of cyclohexanone in an acid medium under ordinary conditions has not been studied to any extent. It is known that when a mixture of equal weights of cyclohexanone and 60% aqueous sulfuric acid is allowed to stand for 24 hours, 2-cyclohexylidenecyclohexanone is formed [2]. It appeared to be of interest to determine the behavior of cyclohexanone in the presence of more concentrated sulfuric acid under the usual conditions.

Results of Experiments on the Autocondensation of Cyclohexanone and 2-Cyclohexylidenecyclohexanone (synthesis time, 8-12 days; temperature, 20-25°)

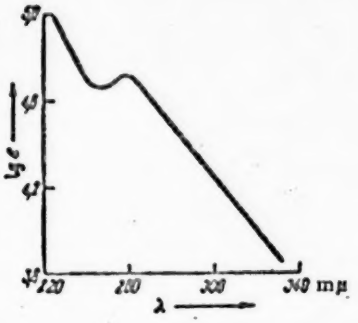
Expt. No.	Ketone	Amount, g	Solvent	Amount, g	Sulfuric acid, g	Yield, g: dodecahydrotriphenylene	Yield, g: $C_{36}H_{52}O_2$	Found*, %: C	Found*, %: H	Mol. wt.
1	Cyclohexanone	240	Methanol	390	460	2,4	80	83,52	10,05	520
2	The same	240	n-Butanol	400	460	12,0	40	83,47	10,13	517
3	The same	240	Water	150	460	1,0	25	—	—	520
4**	The same	240	Methanol	790	240	14,5	2,5	—	—	495
5***	The same	240	Water	100	160	—	10	83,34	9,88	490
6	2-Cyclohexylidenecyclohexanone	350	Methanol	550	650	5,0	120	83,57	10,23	505

* $C_{36}H_{52}O_2$. Calculated, in %: C 83.65; H 10.15. Mol. wt. 516.8.

** The reaction mixture was refluxed for 15 hours [3].

*** Synthesis time was 20 days.

It was found in the present work that a solid product having the empirical formula $C_{36}H_{52}O_2$ (I) is formed by the interaction of cyclohexanone and methanolic sulfuric acid (table). The possible synthesis of (I) under other conditions was also studied with the aim of obtaining data on the structure of (I) and on the reaction by which it is formed. It was found that the same product of the condensation of cyclohexanone, $C_{36}H_{52}O_2$, is formed in the presence of methanol, n-butanol, or water (experiments 1, 2, and 3). It follows, therefore, that the solvent does not participate in the formation of this compound, and that the latter is the product of the autocondensation of cyclohexanone. It should be remarked that we were also able to obtain this same product having the composition



U. v. absorption spectrum of (I) in ethyl alcohol.

$C_{36}H_{52}O_2$ under conditions previously used for the autocondensation of cyclohexanone to 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene; however, the yield was insignificant (about 1%). It was further found that the bicyclic product, 2-cyclohexylidenecyclohexanone, obtained by autocondensation of cyclohexanone [2] is converted in the presence of methanolic sulfuric acid to this same compound $C_{36}H_{52}O_2$ (experiment 6). If the experiment is carried out under the conditions used for the sythesis of 2-cyclohexylidenecyclohexanone and if the reaction time is increased (experiment 5), compound (I) is also formed in addition to the expected product. This compound (I) was shown by fractionation to be the same as the previously prepared compound. Moreover, the tricyclic products of the autocondensation of cyclohexanone 2-[2-(Δ-cyclohexenyl)-cyclohexylidene]cyclohexanone [1], and 2,6-dicyclohexenylcyclohexanone [4] do not form (I) by interaction with methanolic sulfuric acid. Therefore, it may be assumed that autocondensation of cyclohexanone to the compound $C_{36}H_{52}O_2$ proceeds through a stage in which 2-cyclohexylidenecyclohexanone is formed

$$2C_6H_{10}O \rightarrow C_{12}H_{18}O + H_2O, \quad (1)$$

$$3C_{12}H_{18}O \rightarrow C_{36}H_{52}O_2 + H_2O. \quad (2)$$

(I)

A byproduct of the autocondensation of cyclohexanone, dodecahydrotriphenylene, was obtained in experiments 1, 2, 3, and 6. We now turn our attention to the formation of this compound during autocondensation of cyclohexanone (experiment 6). The formation of this compound can be explained by a reaction route which is the reverse of aldol condensation [4-6].

Compound (I) does not hydrolyze when heated to the boiling point at atmospheric pressure with dilute aqueous solutions of acids or bases; it is oxidized to adipic acid when refluxed with concentrated nitric acid; when heated to 250°, compound (I) splits out a molecule of water and forms a compound having the formula $C_{36}H_{50}O$. The compound $C_{36}H_{52}O_2$ does not add hydrogen when subjected to catalytic hydrogenation under the usual conditions in the presence of platinum oxide [7], while the hydrogenation of 2-cyclohexylidenecyclohexanone under these same conditions forms a saturated bicyclic ketone in quantitative yield [8]. Compound I does not form the usual derivatives of carbonyl compounds.

The compound $C_{36}H_{52}O_2$ cannot contain tertiary alcohol groups, since the latter are readily cleaved under the influence of sulfuric acid as a dehydrating agent. In the ultraviolet spectrum of $C_{36}H_{52}O_2$ (Fig. 1), the maximum absorption is found at $\lambda_{max} = 258$ mμ and $\epsilon_{max} = 50300$. Such an absorption maximum is characteristic of α,β,β-trisubstituted α,β-unsaturated carbonyl compounds, and it is close to the absorption maximum for 2-cyclohexylidenecyclohexanone ($\lambda_{max} = 254$ mμ) [9]. The higher molar absorption coefficient as compared to that of 2-cyclohexylidenecyclohexanone can apparently be explained on the basis that (I) contains two carbonyl groups, each of which is conjugated with an ethylenic bond, and the two systems are isolated from each other; otherwise, the absorption maximum would lie in the longer wavelength region (not less than 300 mμ) [10]. Thus, on the basis of reactions (1) and (2), the elemental composition, and u.v. spectrum, the compound $C_{36}H_{52}O_2$ is a hexacyclic diketone containing three double bonds. Two of the three double bonds are conjugated with carbonyl groups, and one is isolated.

EXPERIMENTAL

Preparation of the Diketone $C_{36}H_{52}O_2$ (I). A mixture of 390 g of methanol, 460 g of concentrated sulfuric acid, and 240 g of cyclohexanone (experiment 1) was allowed to stand for 8 days, with stirring from time to time. The reaction mixture was diluted with 6 liters of water, the aqueous layer was separated, and the remainder was dissolved in 300 ml of ether. The resulting white precipitate was filtered off and washed with ether (twice with 50-ml portions). The dried dodecahydrotriphenylene, 2.4 g, melted at 232° (from benzene), and did not depress the melting point of a known sample of dodecahydrotriphenylene [1]. The filtrate was poured slowly and with stirring into 2 liters of methanol. The resulting thick mass was washed with 100 ml of methanol, dissolved in 200 ml

of ether, and again precipitated in 2 liters of methanol. After a third such operation (150 ml of ether and 2 liters of methanol), the resulting solid product was filtered and washed with methanol (twice with 100-ml portions). The product was dried in air, and 80 g of compound (I) was obtained in the form of a yellowish powder with a broad melting range (80-120°, with decomposition); the product was readily soluble in ether, benzene, and pyridine, difficultly soluble in methanol, and insoluble in water.

Compound (I) was isolated in a similar manner in experiments 4, 5, and 6. The separation of (I) in experiments 2 and 3 differed only in that the reaction mixture was first poured into methanol. The results of all experiments and the analytical data are reported in the table.

Fractionation of (I). A solution of 20 g substance (I) (mol. wt 520) in 1500 ml of water was slowly added, with stirring, to the yellow solution. The resulting precipitate was filtered and washed with 50 ml of methanol. The product was dried in air, and 6.5 g of substance (I) was obtained in the form of a slightly yellowish powder with a mol. wt of 525. Another 250 ml of water was added to the filtrate. The precipitate was filtered off, washed, and dried, and 5.5 g of (I) was obtained in the form of a yellowish solid product with a mol. wt of 505. In all of this work, the molecular weights were determined cryoscopically in benzene.

Heating of (I). A 14 g sample of substance (I) was heated for 2 hours at 250°. After cooling, the dark-red, transparent mass was powdered and dissolved in 100 ml of ether, the ether solution was filtered, and a precipitate was formed by slowly stirring-in 500 ml of methanol. The resulting precipitate was filtered off and washed with 50 ml of methanol. Air drying yielded 8 g of a yellow powder.

Molecular weight: found 493; calculated for $C_{36}H_{56}O_4$ 498.8.

Found %: C 86.78; 86.25; H 10.12; 10.33 $C_{36}H_{54}O$. Calculated %: C 86.70; H 10.10

Oxidation of (I). To 250 ml of concentrated nitric acid was slowly added, with cooling, 25 g of (I). The mixture was refluxed for 24 hours, and was then diluted with 250 ml of water. The resulting precipitate was filtered off, washed with water, and dried in air. There was obtained 1 g of a yellow powder which was not investigated further. Evaporation of the filtrate on a water bath yielded 30 g of product. A 10 g sample of this product was stirred with 25 ml of ether, and the almost white precipitate was filtered. There was obtained 4 g of adipic acid with an m.p. of 152° (from water); the product caused no depression of the melting point of a known sample of adipic acid.

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ON THE MECHANISM OF BIMOLECULAR ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

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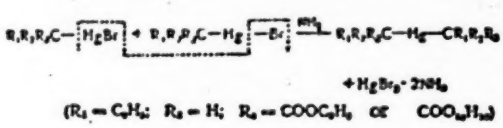
The mechanism of electrophilic substitution at a saturated carbon atom is still in need of clarification. One of the reasons for this lies in the difficulty of studying the sterochemistry and the kinetics of electrophilic substitution reactions.

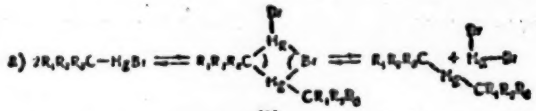
In 1953, one of us together with A. N. Nesmeyanov and S. S. Poddubnaya [1] studied the sterochemistry of the symmetrization of esters of α-bromomercuriphenylacetic acid under the influence of ammonia in chloroform in the cold, and in 1957, one of us and R. E. Mardaleishvili [2] studied the kinetics of this reaction. Thus, the stereochemistry and kinetics of the same electrophilic substitution reaction at a saturated carbon atom were studied for the first time:



$(R_1 = C_6H_5;\ R_2 = H;\ R_3 = COOC_2H_5$ or $COO_2H_{13})$

Since our papers reporting the simultaneous study of the stereochemistry of electrophilic substitution in the case of symmetrization of esters of α-bromomercuriphenylacetic acid [1, 2], there has appeared only a single paper, by Ingolds in 1959 [3], reporting a simultaneous study of the stereochemistry and kinetics of such a reaction—the racemization of di-sec-butylmercury under the influence of $HgBr_2$.

On the basis of the kinetics data (reversible reaction, second order with respect to $R_1R_2R_3CHgBr$ and with respect to ammonia) and sterochemical data (retention of configuration), the mechanism of this reaction can be represented as follows:



(A)

b) $HgBr_2 + 2NH_3 \rightleftarrows HgBr_2 \cdot 2NH_3$

The first stage (a) is a bimolecular electrophilic substitution (S_E2) at a saturated carbon atom.*

*The alternative mechanism (which satisfies the sterochemical and kinetic requirements) is less probable, because the symmetrization reaction proceeds under the influence of the most diverse reagents, irreversibly tying up the

$$a)\ R_1R_2R_3CHgBr + NH_3 \rightleftarrows R_1R_2R_3CHgBr\cdot NH_3,$$

$$b)\ 2R_1R_2R_3CHgBr\cdot NH_3 \rightleftarrows (R_1R_2R_3C)_2Hg + HgBr_2\cdot(NH_3)_2$$

The present authors and Yan-tsei U [5] have studied the kinetics of another electrophilic reaction at a saturated carbon atom – an isotope exchange reaction between esters of α-bromomercuriphenylacetic acid and mercuric bromide labeled with Hg^{203}.

$$R_1R_2R_3CHgBr + Hg^*Br_2 \rightleftarrows R_1R_2R_3CHg^*Br + HgBr_2,$$

($R_1 = C_6H_5$; $R_2 = H$; $R_3 = COOC_2H_5$ or $COOC_{10}H_{19}$)

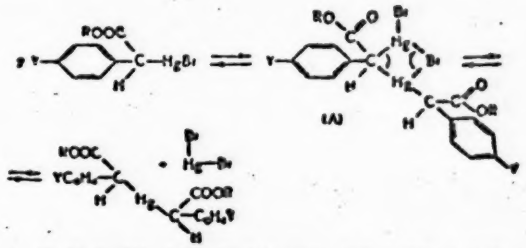
The over-all reaction is second order, and it possible proceeds by an analogous two-stage mechanism, the first step (a) of which is identical to the first step of the symmetrization reaction:

$$(a)\ 2R_1R_2R_3CHgBr \rightleftarrows R_1R_2R_3C-Hg-CR_1R_2R_3 + HgBr_2,$$

$$(b)\ (R_1R_2R_3C)_2Hg + Hg^*Br_2 \rightleftarrows R_1R_2R_3CHg^*Br + R_1R_2R_3CHgBr.$$

In all probability, reactions of the above types can proceed through the transition state (A), and this also holds in the case of other organomercury salts having a relatively weak C–Hg bond.

We have now studied the effect of structural factors on the rate of a bimolecular electrophilic substitution at a saturated carbon atom, using as a model reaction the symmetrization of compounds of the type of $p\text{-}YC_6H_4CH^*(HgBr)COOR$ under the influence of ammonia in chloroform. The first, slow stage of this reaction evidently proceeds through a transition state of the type of (A).



1. Y=H; R=CH_3, C_2H_5, iso-C_3H_7, tert-C_4H_9, n-C_5H_{11}, L-$C_{10}H_{19}$
2. Y=Cl, Br, H_3C; R=C_2H_5

It is possible to visualize the significant effect of the nature of the substituent R on the rate of symmetrization through the following reaction rate constants, which were calculated by means of a previously proposed method [2]:

R	CH_3	C_2H_5	iso-C_3H_7	tert-C_4H_9	n-C_5H_{11}	$C_{10}H_{19}$ (L-menthyl)
K_2 ml/mole·sec	181,5	110	25,9	insignificantly small	10,2	6,9

The reaction rate of the methyl ester was more than 25 times the reaction rate of the L-menthyl ester.

Naturally, the effect of the nature of R on the reaction rate is the sum of polar and steric factors.

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mercuric bromide. Thus, the present authors and L. R. Filippenko [4] found that esters of α-bromomercuriphenylacetic acid (as well as other organomercury compounds with a labile mercury) readily undergo symmetrization under the influence of diphenylmercury:

$$2R_1R_2R_3C-HgBr + (C_6H_5)_2Hg \rightarrow (R_1R_2R_3C)_2Hg + 2C_6H_5HgBr.$$

The intermediate formation of an $R_1R_2R_3CHgBr\cdot(C_6H_5)_2Hg$ complex in this reaction is improbable, particularly, because this contradicts the stereochemistry of the reaction.

The nature of substituent Y also has an effect on the symmetrization rate, as may be seen from the values of the corresponding rate constants for compounds of the type $p\text{-}YC_6H_4CH(HgBr)COOC_2H_5$:

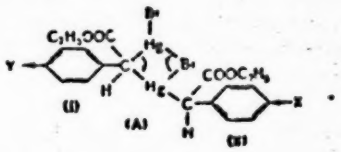
Y	Cl	Br	H	CH_3
K_2, ml/mole·sec	470	400	110	0

Substitution of a chlorine for the hydrogen atom in the para-position of the benzene ring accelerates the reaction by more than a factor of five, and substitution of a methyl group practically stops the reaction. Naturally, in the case of bimolecular nucleophilic substitution in analogous systems, the effect of substitutents on the reaction rate is the reverse.*

Since the effect of the Y substituent on the rate of this reaction apparently depends on purely polar factors, on the basis of the data presented above it may be concluded that repulsion of electrons from the reaction center (the saturated carbon atom) facilitates bimolecular electrophilic substitution reactions (S_E2). This fact indicates that even in bimolecular substitution, the more important role is played by rupture of the old bond, not formation of the new bond. This circumstance connects the bimolecular mechanism S_E2 with the monomeric dissociation mechanism S_E1, since in the latter, rupture of the old bond is the step which determines the over-all rate of the process.

Our results show that electrophilic substitution at a saturated carbon atom proceeds in a considerably more complex manner than has previously been supposed on the basis of simple limiting cases of S_E1 and S_E2.

Since not only the old C—Hg bond but also the old Hg—Br bond is ruptured in the transition state (A), it would be expected that the symmetrization reaction would proceed more rapidly when dissimilar molecules of organometry salts containing different substituents in the para-position of the benzene ring reacts with each other. If, for example, Y is an electron-acceptor and X an electron-donor substituent, the transition state (A)



will be formed more easily than in the case when similar molecules react. Rupture of the old C—Hg bond is facilitated in the first of the reaction molecules, and rupture of the Hg—Br bond is facilitated in the second.

Cosymmetrization of this type was carried out with the following pairs of compounds: X = H, Y = Cl, X = Br; Y = H, X = CH_3. The initial reaction rate was calculated for each case. The following result was obtained in this manner. The over-all rate of the process in the first two case proved to be greater than the sum of the initial rates for the remaining components when used in the same concentrations, exceeding the individual rates of the most rapidly reacting components. In the case of X = CH_3, the results proved to be most interesting. While symmetrization does not proceed to any extent in the case of the p-methyl-substituted ester, when this ester is mixed with the unsubstituted ester, symmetrization does take place to a specific extent, though it does not go to completion. The over-all rate of the process is greater than for the unsubstituted ester in the same concentration.

One interesting and important question is the effect on reaction rate of the addition of different compounds which do not take part in the reaction. The effect of the addition of polar molecules on the rate of nucleophilic reactions has been studied by Ingolds [10-14] and by Swain [15, 16], who, on the basis of their results, arrived at diametrically opposed conclusions as to the nature of this phenomenon.

We studied the effect of such an addition on S_E2 reactions. It was found that the addition of polar reagents to the reaction mixture significantly accelerated symmetrization of esters of α-bromomercuriphenylacetic acid. Table 1 presents the second-order rate constants, which were calculated from the half-life of the reaction, based on formation of the product, at an initial α-bromomercuriphenylacetic ester concentration of $6.8 \cdot 10^{-5}$ mole/ml, an ammonia concentration of $\sim 1 \cdot 10^{-3}$ mole/ml, and different concentrations of the added materials.

* For example, in the case of reactions of substituted benzyl chlorides with amines [8], azides [7], or in Finkelstein substitution [8, 9].

Added material	C·10³, mole/ml*	$\tau_{1/2}$, sec	K_2, ml/mole·sec
Nitromethane	0	136	108
	0.469	75	197
	0.937	57	258
Nitrobenzene	0	170	86.7
	0.902	128	114.8
Methyl alcohol	0	136	108
	0.309	110	133
	0.618	93	158.5

* On the average, this was $^1/_{25}$ of the amount of solvent.

It was also shown that the solvent itself (chloroform, in our case), being a polar molecule, has an accelerating effect on the reaction. This was shown by carrying out the reaction in an inert solvent – benzene – with the addition of various amounts of chloroform.

A similar result was obtained during a study of the rate of isotope exchange between $C_6H_5CH(HgBr)COOC_2H_5$ and $Hg^{203}Br_2$. Thus, while the percent exchange in benzene was insignificantly low, when the solvent was changed to one having appreciable polarity, for example 70% aqueous dioxane, the rate increased by a factor of nine.

The addition of acids and also of bases had an accelerating effect on the rate of the isotope exchange reaction between α-bromomercuriphenylacetic esters and $Hg^{203}Br_2$. For example, we found that the addition of pyridine has an extremely strong effect on the rate of isotope exchange of L-menthyl α-bromomercuriphenylacetate in acetone (reactant concentration of 0.03 mole/ml) at 50°. While in the absence of an added material there was only 1% exchange in 6 hours, the addition of pyridine in an amount of five parts by weight of the acetone led to 35% exchange in 3 hours, and the addition of ten parts by weight promoted 92% exchange in 4.5 hours.

It is still an open question as to whether the polar additives enter into the transition state (i.e., whether there is a specific kinetic course through the additive), or whether their role amounts to a change in the polarity of the reaction medium, which, in turn, has an effect on the reaction rate. This question is subject to further investigation.

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ZIRCONIUM NIOBATE AND TANTALATE

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Literature information on zirconium niobates is limited to a description of the compound $ZrO_2 \cdot 5Nb_2O_5$, which has been prepared by interaction of zirconium chloride and potassium niobate in solution [1] and also by fusing a mixture of ZrO_2 and Nb_2O_5 with NaF [2]. That this is an individual compound has not been confirmed by any physicochemical method. Measurement of the density gave a value of 5.14 at 17-18°. Zirconium tantalates have not been described in the literature.

The present work was devoted to a study of conditions required for the formation of zirconium niobate and tantalate. Mixtures of zirconium and niobium hydrated oxides were prepared with different mole ratios of ZrO_2 to Nb_2O_5 (2:1, 1:1, and 1:2). The original hydrated oxides were dried at 100° and carefully ground and mixed. The resulting mixtures were sintered at 1300° in a Silit furnace for a prolonged time (40-60 hours). In addition to the mixtures, the individual hydrated oxides were calcined under the same conditions. X-ray patterns were obtained under the same conditions (with a RKD-57 camera, using an iron anode) for all of the products obtained. The x-ray patterns were measured with a comparator which had a precision of 0.05 mm. Line intensities were evaluated visually by the five-point system. The results of the x-ray measurements were in good agreement with the literature data [3-5]. The x-ray pattern of the mixture of ZrO_2 and Nb_2O_5 in a 2:1 ratio had no lines characteristic of ZrO_2 or Nb_2O_5 (Fig. 1), which indicates the formation of a new phase. In addition to the lines characteristic of the compound with a 2:1 ratio of the oxides, the patterns of the other mixtures (1:1 and 1:2) had lines characteristic of Nb_2O_5. No new lines characteristic of compounds corresponding to other oxide ratios were found.

In a manner similar to the synthesis of zirconium niobate, zirconium tantalate was synthesized by sintering under the same conditions a mixture of the hydrated oxides of zirconium and tantalum, in a mole ratio of ZrO_2 to Ta_2O_5 of 2:1. The x-ray pattern of this mixture after sintering had no lines characteristic of ZrO_2, but there were a few lines which could be ascribed to free Ta_2O_5. However, the absence of the three strong Ta_2O_5 lines, which are good indications of a rhombohedral lattice with the axes $a = 6.175 \pm 0.125$ kX, $b = 3.649 \pm 0.003$ kX, and $c = 3.891 \pm 0.005$ kX (cf. data of reference [5]), makes it possible to conclude that the correspondence with the free Ta_2O_5 lines is purely coincidental. Thus, the sintered products in this case represent a new phase. It should be noted that the interaction of ZrO_2 takes place much more readily with Nb_2O_5 than with Ta_2O_5. The formation of zirconium niobate was observed even when the mixture was heated to 1000° over a six-hour period, while zirconium tantalate was formed only after prolonged (40 hours) soaking of the mixture at 1300°.

In view of the insignificant volatility of the original oxides at their interaction temperatures, the ratios $ZrO_2 : Nb_2O_5$ and $ZrO_2 : Ta_2O_5$ in the resulting compounds should not differ from the original values and should obviously correspond to the formula $2ZrO_2 \cdot R_2O_5$ or $(ZrO)_2R_2O_7$. These compounds were analyzed for zirconium content as follows. A weighed sample of zirconium niobate was dissolved by heating in concentrated H_2SO_4, and, after dilution of the solution, zirconium was precipitated as the phosphate. The niobium was held in solution by the addition of hydrogen peroxide. The zirconium pyrophosphate precipitate was calcined at 900° and weighed.

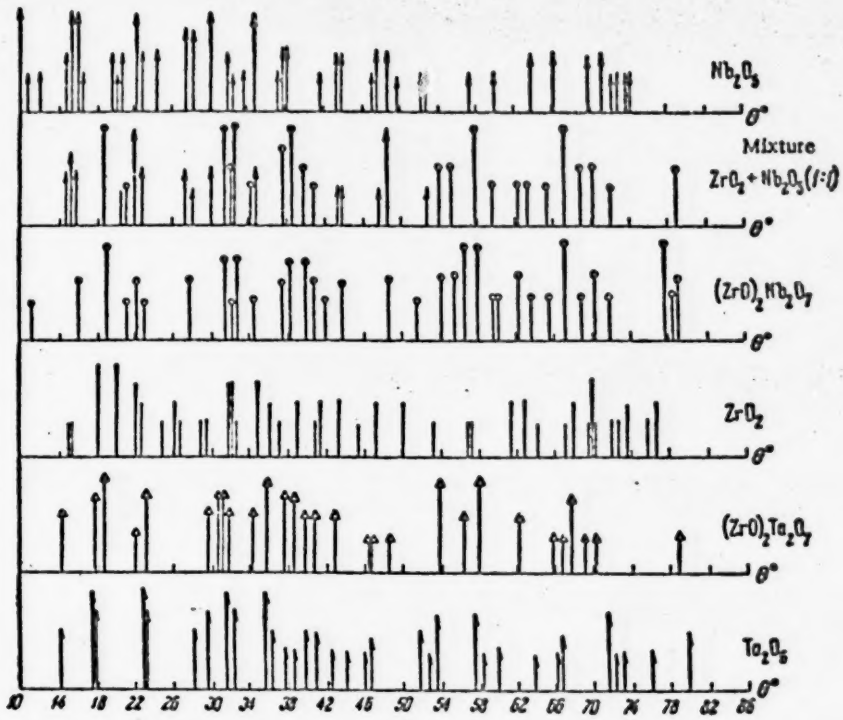

Fig. 1. Schematic representation of the x-ray patterns.

Fig. 2. Heating curves. A) $(ZrO)_2Nb_2O_7$ (average heating rate, 10°/min); B) $(ZrO)_2Ta_2O_7$ (average heating rate, 8°/min).

In the analysis of the zirconium tantalate, the material was decomposed by evaporation with concentrated H_2SO_4 two or three times. The precipitate was treated by boiling with a 5% solution of NaOH to convert the sulfates to hydroxides. The zirconium hydroxide was dissolved in 2N HCl by heating the mixture, and the tantalum was completely retained in the precipitate. Zirconium hydroxide was precipitated from the hydrochloric acid solution, and the precipitate was calcined at 900° and weighed.

The analyses showed the following percentage contents of ZrO_2 (averages of two to three experiments):

	Found	Calc. for $(ZrO)_2R_2O_7$
Zirconium niobate	49.40	48.11
Zirconium tantalate	36.20	35.80

Zirconium niobate and tantalate are white, finely crystalline compounds. The great number of lines (about 50) on the x-ray patterns of these compounds indicate a low symmetry of the crystal lattice. The high values of the glide angles are in agreement with the relatively low density values: 5.70 for $(ZrO)_2Nb_2O_7$ and 7.82 for $(ZrO)_2Ta_2O_7$. (The density determinations were carried out pycnometrically at 25°.)

In order to confirm that these compounds were chemical individuals and also with the aim of comparing their properties, their melting points were determined, their thermal stabilities were investigated, and their behavior toward certain chemical reagents was studied. Fusion of the zirconyl niobate and tantalate was carried out

TABLE 1

Chlorination of Zirconyl Niobate and Tantalate and Mixtures of the Original Oxides (2:1) with Carbon Tetrachloride. Sample Weight 0.2 g, Particle Size < 100 μ, Chlorination Time 30 minutes

Expt. series	CCl_4 feed rate g/cm².hour	Substance	Loss in weight, %			
			at 500°	at 550°	at 600°	at 650°
1	0,05	$(ZrO)_2Nb_2O_7$	2,3	5,4	6,6	
		Mixt. ZrO_2 & Nb_2O_5 (2:1)	7,1	14,9	24,3	
2	0,12	$(ZrO)_2Ta_2O_7$	—		4,8	6,9
		Mixt. ZrO_2 & Ta_2O_5 (2:1)	—		16,5	31,8
3	0,10	$(ZrO)_2Nb_2O_7$	4,9	11,7	14,4	
		$(ZrO)_2Ta_2O_7$	—	2,5	4,0	

TABLE 2

Behavior of Zirconyl Niobate and Tantalate Toward Reagents. Sample Weight 0.1 g, Temperature 85-90°, Treatment Time 4 Hours.

Reagent	Amt. of dissolved material, g/100 ml reagent	
	$(ZrO)_2Nb_2O_7$	$(ZrO)_2Ta_2O_7$
HCl, 36%	0,0320	0,0000
H_2SO_4, 94%	0,0920	0,0000
H_2F_2, 25%	0,1008	0,0610
NaOH, 40%	0,0266	0,0082

in a type MVP-3 high-frequency furnace, which is suitable for operations under vacuum or at atmospheric pressure. The temperature was measured with an "Opir-09" optical pyrometer. Fusion of the material was detected visually. By means of these experiments, it was established that the melting points of zirconyl niobate and tantalate are 1700 ± 20° and 1730 ± 20°, respectively. According to data from x-ray phase analyses, both compounds melted without decomposition and underwent no phase transformations over the temperature interval of 20 to 1400°. The latter was confirmed by a study of the thermal stability of the compounds with a Kurnakov pyrometer. The heating curves for $(ZrO)_2Nb_2O_7$ and $(ZrO)_2Ta_2O_7$ are presented in Fig. 2.

The rate of interaction of zirconyl niobate and tantalate with CCl_4 vapors was studied. For purpose of comparison, the corresponding mixtures of ZrO_2 with Nb_2O_5 (2:1) and ZrO_2 with Ta_2O_5 (2:1) were chlorinated under the same conditions. The conditions under which the experiments were carried out differed only in the CCl_4 feed rate and in the surface areas of the preparations. The carbon tetrachloride was fed to the quartz reaction tube in a stream of nitrogen, which was passed at a constant rate through a flask filled with CCl_4. The chlorination was carried out over the temperature interval of 500-650° for a period of 30 minutes. Upon completion of an experiment, the residual material was weighed, and, in some cases, the ZrO_2 content was determined. In addition, x-ray phase analysis of the residual material was carried out. The results obtained are presented in Table 1; the values represented averages of three or four determinations.

It should be noted that zirconyl niobate and tantalate chlorinate three to four times more slowly than do the corresponding oxide mixtures. Zirconyl tantalate is more stable with respect to the chlorinating agent; in contrast to zirconyl niobate, the tantalate undergoes no chlorination at 500°. According to chemical and x-ray phase analysis data, the major portion of the zirconyl niobate and tantalate underwent no change during the chlorination process.

The action of HCl (36%), H_2F_2 (25%), H_2SO_4 (94%) and NaOH (40%) on zirconyl niobate and tantalate was tested in order to determine the stability of the niobate and tantalate toward solutions of various reagents. A weighed sample (0.1 g) of the material was treated with 50 ml of the reagent for a period of 4 hours at 85-90°. The residue was washed with water, dried at 100°, and weighed and analyzed by x-ray phase analysis. It was established that both compounds have high stability with respect to the reagents tested (Table 2). The best solvent was the concentrated solution of H_2F_2. The zirconyl tantalate was more stable than the niobate. In contrast to the latter, zirconyl tantalate was practically insoluble in hot solutions of concentrated HCl and H_2SO_4 and in a mixture of ammonium sulfate and sulfuric acid, and it did not fuse with sodium pyrosulfate, K_2CO_3, or sodium

peroxide. While zirconyl niobate dissolved readily when heated to 220° in concentrated H_2SO_4, decomposition of the tantalate occurred only when the material was evaporated in concentrated H_2SO_4. During the action of the reagents indicated above, the undissolved part of the compounds did not undergo any changes, as indicated by x-ray phase analysis. Thus, zirconyl niobate and tantalate are chemically very stable.

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PREPARATION OF HIGHER ALIPHATIC KETONES BY DEHYDROGENATION OF SECONDARY ALCOHOLS

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We previously [1] demonstrated the possibility of synthesizing higher aliphatic ketones by oxidation of higher secondary alcohols, which, in their turn, were obtained by direct oxidation of paraffins in the presence of boric acid [2]. The possibility of preparing ketones by dehydrogenation of these higher alcohols was also reported [1].

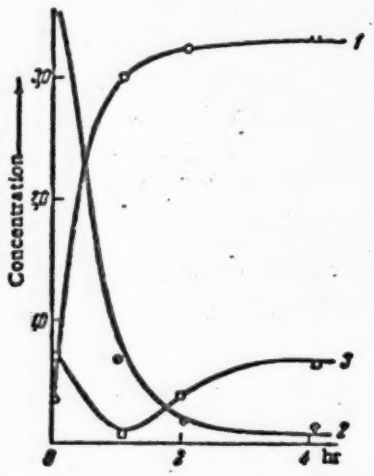

Fig. 1. Kinetics of dehydrogenation of secondary alcohols on skeletal nickel catalyst (185°, residual pressure 33 mm Hg). 1) Ketones; 2) alcohols; 3) unsaturated compounds.

There are reports in the literature on the preparation of lower aldehydes and ketones by this method. The reaction is normally carried out in the vapor phase over catalysts which contain iron, zinc, copper, nickel, platinum, etc. [3]. It was also shown that with an increase in the molecular weight of the alcohols, the dehydrogenation does not proceed smoothly at all and is complicated by dehydration [4]. Higher alcohols can also be dehydrogenated in the liquid phase over a Raney catalyst [5].

In the present work we give the results of an investigation of the dehydrogenation of higher secondary alcohols for preparing the corresponding ketones on an industrial skeletal nickel catalyst.

The higher secondary alcohols were dehydrogenated in the liquid phase in a flask with a stirrer and a condenser. The mixture was heated with a gas burner and the reaction temperature controlled with a thermometer. When the reaction was carried out in vacuum, the system was connected to a vacuum pump. The reaction product (dehydrogenation product) was analyzed by the usual procedure. The acid, ester, hydroxyl, carbonyl, and iodine numbers were determined. The amount of catalyst used in all experiments was 10% of the weight of alcohols. For the dehydrogenation we used industrial alcohols with the following constants: d^{20}_4 0.8486; $n^{20}D$ 1.4496; b.p. 125-170° (1 mm Hg) (C_{16}–C_{18}); solid. p. +8.0°; acid number 1.1; ester number 3.4; hydroxyl number 220.0; carbonyl number 20.0; iodine number 10.0; hydrocarbon content 6 weight %. An examination of the kinetic curves for the reaction on this catalyst (185°, residual pressure 33 mm Hg) shows that the dehydrogenation of alcohols in the liquid phase proceeded at a high rate and was practically complete in 2 hours, giving a degree of alcohol conversion of up to 95 mol. % (see Fig. 1).

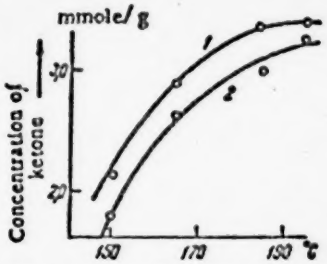

Fig. 2. Effect of temperature and pressure on the formation of ketones by dehydrogenation of secondary alcohols on a skeletal nickel catalyst (reaction time 2 hours). 1) Residual pressure 30 mm Hg; 2) atmospheric pressure.

Vigorous evolution of hydrogen was observed in the initial period. There was a simultaneous decrease in the iodine number of the product and this is apparently explained by the hydrogenation of unsaturated compounds present in the original alcohols. Subsequently there was a certain increase in the iodine number as a result of dehydration of alcohols. Chromatographic analysis of the dehydrogenation product on silica gel showed that the hydrocarbon content increased from 6-10 weight %.

The acid and ester content of the reaction products hardly differed from that of the original alcohols.

Experiments were then carried out to determine the effect of temperature and pressure on the dehydrogenation of alcohols.

The curves presented in Fig. 2 show that the rate of dehydrogenation of alcohols increases with a rise in temperature. A reduced pressure (residual pressure of 33 mm Hg) promoted the reaction studied.

The product obtained by dehydrogenation of higher secondary alcohols was freed from small amounts of unreacted alcohols by esterification of the latter with boric acid. The compounds which did not react with boric acid were distilled from the boric esters formed in a Claisen flask at a residual pressure of 7 mm Hg. We obtained a distillate boiling over a range 115-200° with the constants: d^{20}_4 0.8350; $n^{20}D$ 1.4440; solid. p. +14.5°; carbonyl number 190.0; iodine number 4.6. Freeing this product from hydrocarbons by chromatography on silica gel yielded a fraction of higher aliphatic ketones with d^{20}_4 0.8362; $n^{20}D$ 1.4446; carbonyl number 202.0. The ketone yield was 85 weight % on the starting alcohols.

Thus, the investigation showed that it is possible to obtain higher aliphatic ketones in high yield by dehydrogenation of higher secondary alcohols in the liquid phase on skeletal nickel catalysts.

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FORMATION OF A LINEAR ISOPRENE DIMER ON THE COMPLEX CATALYST (iso-C_4H_9)$_3$Al + $TiCl_4$

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(Presented by Academician L. L. Knunyants, December 18, 1959)

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The thermal dimerization of isoprene leads exclusively to cyclic compounds, as was conclusively demonstrated by I. N. Nazarov et al. [1], and then confirmed by American investigators [2]. The possibility of linear dimerization of isoprene has been discussed repeatedly [3-6] but up to the present there has evidently been no case where linear dimers have been isolated in a discrete state and their structure has not been determined.

Thus, in [5] it was reported that in the presence of an aluminosilicate catalyst, isoprene gives a very low yield of a linear dimer, which was not isolated in a pure state by the authors (it contained traces of dihydro dimer) and did not form an adduct with maleic anhydride. In [6], the dimerization of isoprene under the action of sulfuric and phosphoric acids yielded a mixture of dimeric products, which was shown to contain a linear dimer by isolation of 2,6-dimethyloctane after hydrogenation of the mixture over a platinum catalyst at 180°. The formation of trimeric compounds was reported in the same work, but nothing was stated on their structure. It was shown recently [7] that under the action of a complex catalyst, isoprene is polymerized to cis-1,4-polyisoprene, which is similar to natural rubber in properties.

In the present work we found that on the same catalyst but with a change in reaction conditions, isoprene forms largely dimeric, trimeric, and tetrameric products and only a very small amount of polymer. We carried out the reaction in toluene at 75-85° with a catalyst prepared with molar ratios of (iso-C_4H_9)$_3$Al to $TiCl_4$ equal to 2.25-3.25 to 1. The reaction proceeded rapidly under these conditions and the isoprene reacted practically completely. With a fall in reaction temperature or a decrease in the ratio of (iso-C_4H_9)$_3$Al to $TiCl_4$, the amount of copolymer increased. With an increase in the ratio of (iso-C_4H_9)$_3$Al to $TiCl_4$, the reaction rate fell considerably or the reaction did not begin at all. This indicates that the reaction was actually catalyzed by the complex catalyst. Dimeric and trimeric products were formed in approximately equal amounts while less than 10% of polymer was obtained.

Thus, 136 g (200 ml) of carefully dried isoprene was added over a period of 2 hours with stirring at 75-80° to 100 ml of toluene, containing a catalyst prepared from 5.2 g of (iso-C_4H_9)$_3$Al and 1.8 g of $TiCl_4$. Distillation of the reaction products yielded 55 g of a mixture of dimers, 49 g of a mixture of trimers, and 12 g of a mixture of tetramers, and 12 g of polymer remained. In the present work we investigated mainly the dimeric compounds. Fractionation of the mixture of dimers on a column yielded:

1. "Lebedev's hydrocarbon", i.e., 2,4-dimethyl-4-ethenyl-1-cyclohexene with b.p. 48-48.5° at 14 mm, $n^{20}D$ 1.4646, d^{20}_4 0.8321 (literature data [8]: b.p. 44° at 9 mm, $n^{20}D$ 1.4658, d^{20}_4 0.8331).

2. A linear isoprene dimer (main product) to which we ascribed the structure of 2,6-dimethyl-1,3,6-octatriene, $CH_2 = C(CH_3)CH = CH-CH_2-C(CH_3) = CH-CH_3$, on the basis of its reactions and this had b.p. 57-58° at 12 mm, $n^{20}D$ 1.4794; d^{20}_4 0.7988.

Found %: C 88.22; 88.10; H 11.80; 11.85 $C_{10}H_{16}$. Calculated %: C 88.23; H 11.76

3. A small amount of what were apparently eight-membered dimers with b.p. 66-68° at 12 mm, $n^{20}D$ 1.4880 (literature data [1]: b.p. 83-83.5° at 26 mm, $n^{20}D$ 1.4885).

The linear isoprene dimer that we obtained differed from known natural linear dimers, myrcene and ocimene. In the hydrogenation of the linear dimer over the catalyst Pd/$BaSO_4$ at room temperature, 3 moles of hydrogen was absorbed per mole of dimer and this yielded 2,6-dimethyloctane with b.p. 158-159°; $n^{20}D$ 1.4103; d^{20}_4 0.7289 (literature data [9]: b.p. 158-159.5°, $n^{20}D$ 1.4100; d^{20}_4 0.7287). Reduction of the dimer with sodium in alcohol yielded the dihydro compound $C_{10}H_{18}$ with b.p. 162.5-163.5°; $n^{20}D$ 1.4458; d^{20}_4 0.7795; MR found 47.44, calculated 47.45.

Found %: C 86.74; 86.76; H 12.91; 12.89 $C_{10}H_{18}$. Calculated %: C 88.95; H 13.04

The dihydro compound, which was apparently 2,6-dimethyl-2,6-octadiene, was readily oxidized in air. The linear dimer reacted vigorously with maleic anhydride to give a high yield of an adduct with b.p. 167-168° at 5 mm, $n^{20}D$ 1.5050.

Found %: C 71.83; 71.74; H 7.78; 7.65 $C_{14}H_{18}O_3$. Calculated %: C 71.79; H 7.69

Alkaline hydrolysis of the adduct yielded a dicarboxylic acid with m.p. 137-138° (from acetonitrile).

Found %: C 66.58; 66.45; H 8.00; 8.07 $C_{14}H_{22}O_4$. Calculated %: C 66.66; H 7.98

When the dicarboxylic acid obtained was hydrogenated over Pd/$BaSO_4$ at room temperature, 2 moles of hydrogen was absorbed per mole of acid. Ozonization of the linear dimer with subsequent treatment with hydrogen peroxide yielded formic and acetic acids, indicating the presence of the groupings $CH_3CH=C<$ and $CH_2=C<$ in the dimer. Ozonization of the adduct of the dimer and maleic anhydride and subsequent reduction of the ozonide with zinc yielded acetaldehyde. This result indicated that the conjugated system of double bonds in the dimer was at the methylene group end, i.e. $CH_2=C-C=C<$. All the data obtained establish quite conclusively that the dimer was 2,6-dimethyl-1,3,6-octatriene.

A preliminary study of the mixture of trimeric compounds also showed that it consisted of both linear and cyclic products, but we have not yet established their structures. For example, from this mixture we isolated a fraction with b.p. 117-118° at 8 mm; $n^{20}D$ 1.4908; d^{20}_4 0.8454; MR found 69.86; calculated 69.60 (for an aliphatic sesquiterpene) MR found 67.87 (for a monocyclic sesquiterpene).

Found %: C 88.14; 88.11; H 11.62; 11.58 $C_{15}H_{24}$. Calculated %: C 88.23; H 11.76

However, this fraction was not a pure aliphatic trimer as on hydrogenation it absorbed slightly less hydrogen than the calculated amount for four double bonds. It reacted with maleic anhydride to form an adduct with the composition $C_{19}H_{26}O_3$ with b.p. 193-195° at 5 mm; $n^{20}D$ 1.5121.

Foudn %: C 75.31; 75.29; H 8.50; 8.48 $C_{19}H_{26}O_3$. Calculated %: C 75.49; H 8.60

On hydrogenation, the adduct absorbed 3 moles of hydrogen per mole of adduct. The investigation of the structure of the trimeric and tetrameric compounds will be continued.

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SYNTHESIS OF POLYMERIZABLE UNSATURATED ORGANOMERCURY COMPOUNDS

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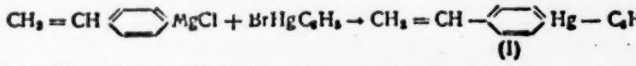
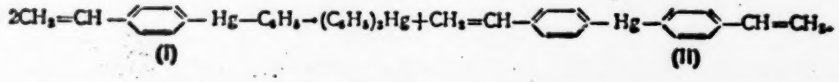
Unsaturated organomercury compounds are attracting the attention of investigators at the present time. The first such compounds synthesized were allyl [1] and isopropenyl [2] compounds of mercury and also mercury derivatives of stilbene [3], and various vinyl derivatives of mercury [4-6], and perfluorodivinylmercury [7] were obtained comparatively recently. Nonetheless, there is no information on the capacity of these unsaturated organomercury compounds to polymerize. From a few literature data [8, 9], it is known that mercury-containing polymers, which are stable up to 250-300°, exist. We synthesized for the first time a vinyl derivative of diphenylmercury, which is capable of polymerization and copolymerization [10]. Thus, the reaction of p-vinylphenylmagnesium chloride and phenylmercuric bromide in tetrahydrofuran yielded crystalline phenyl-p-vinylphenylmercury (I) according to the equation:

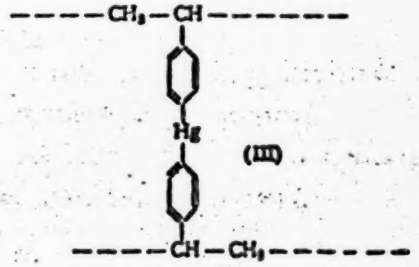


Compound (I) readily polymerized and copolymerized without initiators or in the presence of azoisobutyrodinitrile. The use of benzoyl peroxide, cationic polymerization catalysts, and complex catalysts is excluded (even at low temperatures) as they react chemically with the monomer (I).

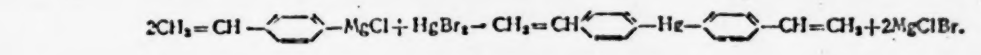
During the polymerization of (I), phenyl-p-vinylphenylmercury (I) disproportionates with the formation of diphenylmercury and a new unsaturated organomercuty compound, namely, bis-p-vinylphenylmercury (II), by the equation:



Compound (II) polymerized very readily with the formation of an insoluble and infusible cross-linked polymer (III), which decomposed at temperatures above 250° with the liberation of metallic mercury.



To demonstrate the accuracy of the above hypothesis, bis-p-vinylphenylmercury was synthesized (it was a crystalline material) by the reaction of p-vinylphenylmagnesium chloride with mercuric bromide in tetrahydrofuran:



Monomer (II) polymerized readily with the formation of a polymer with the same structure (III) as in the case of the disporportionation product of phenyl-p-vinylphenylmercury.

EXPERIMENTAL*

Phenyl-p-vinylphenylmercury (I) was synthesized in dry, freshly distilled tetrahydrofuran in a stream of nitrogen. From 1.94 of magnesium and 5.6 g of p-chlorostyrene in 30 ml of tetrahydrofuran and 10 g of dry phenylmercuric bromide we obtained a colorless, viscous oil, which solidified when cooled to −40°. Three recrystallizations from ethyl alcohol yielded colorless crystals with m.p. 84-86°, which were soluble in benzene and alcohol. The yield was 2.7 g (25% of theoretical).

Found %: C 43.99; H 3.46; Hg 52.35 $C_{14}H_{12}Hg$. Calculated %: C 44.15; H 3.16; Hg 52.70

Treatment of phenyl-p-vinylphenylmercury with an alcohol solution of HCl at 0 to +20° yielded styrene, C_6H_5HgCl, and $HgCl_2$, but when the temperature was reduced to −5°, styrene and C_6H_5HgCl were formed.

Bis-p-vinylphenylmercury (II) was synthesized under the same conditions as (I). From p-vinylphenylmagnesium chloride and mercuric bromide we obtained colorless crystals with m.p. 140-145°, which were soluble in alcohol and benzene. The yield was 30% of theoretical.

Found %: C 46.85; H 3.81; Hg 48.81; 49.42 $C_{16}H_{14}Hg$. Calculated %: C 47.22; H 3.44; Hg 49.33

Block polymerization of (I) in a nitrogen atmosphere in the absence of initiators, or polymerization in xylene solution in the presence of 0.3% of azoisobutyrodinitrile as initiator, yielded a friable, pale-yellow, transparent polymer (III), which was insoluble in all organic solvents. The polymer yield was 50%. After the polymer had been treated with solvents, the solution yielded white crystals of diphenylmercury with m.p. 120-121°. The polymer (III) was dried to constant weight and analyzed.

Found %: C 47.99; H 4.05; 3.99; Hg 48.38 $(C_{16}H_{14}Hg)_n$. Calculated %: C 47.22; H 3.44; Hg 49.33

When heated to 250°, the polymer darkened and with further heating to 270-300°, it decomposed with the evolution of metallic mercury. Polymerization of (II) under the same conditions as (I) formed a friable, light-yellow, transparent, infusible polymer, which corresponded in properties and composition to polymer (III) obtained from (I).

(I) and (II) copolymerized with styrene to form clear, colorless, insoluble masses.

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* Original Russian pagination. See C. B. Translation.

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STRUCTURE OF MONOMERIC ARSENO COMPOUNDS

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(Presented by Academician A. N. Nesmeyanov, October 12, 1959).

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All the arseno compounds described in the literature may be divided into two groups. Compounds of the first group are colored, amorphous, and cannot be recrystallized or distilled. Some compounds of this group do not dissolve in any solvents (for example, arsenomethane polymers), while others dissolve in suitable solvents to form more or less viscous solutions (for example, Salvarsan). According to recent data [1], the structure of compounds of this group is expressed by the formula:

(I) $x-As(R)-(-As(R)-)_{n-2}-As(R)-x$, $x = HO, I, Cl$;

$R = CH_3-$ arsenomethane polymers

$R = -C_6H_3(OH)(NH_2)-$ Salvarsan

Depending on the preparation conditions, the value of n may vary over the range from 7-8 to 40-50 and therefore, some polymeric arseno compounds form solutions of comparatively low viscosity (for example, when n = 8, and $R = -C_6H_3(OH)(NH_2)$. The molecular weight of the polymer ≈1500). When x = OH, the polymers may undergo dehydration, even in aqueous solutions, and this leads to an increase in the molecular weight and, naturally, the viscosity of the solution.

$$m\,HO(-As(R)-)_n-OH \rightleftharpoons HO(-As(R)-)_n-[-O-(-As(R)-)_n-]_{m-2}-O-(-As(R)-)_n-OH + \frac{m-2}{2}H_2O.$$

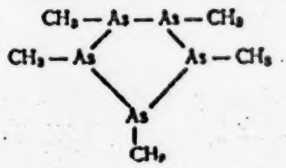
The reaction is reversible and this explains the variable viscosity of Salvarsan solutions. The molecular weight of Salvarsan with a sufficiently high value of n may, with appropriate treatment, reach a value of the order of 1,000,000 [2]. Arsenomethane polymers [3] are insoluble and may be obtained only under conditions when terminal groups may be formed [4].

Arseno compounds of the second group are colorless and crystallize readily (for example, arsenobenzene, p-arsenoanisole, etc) or may be distilled (arsenomethane). While compounds of the first group are polymers, compounds of the second group clearly have the characteristics of monomeric compounds. At one time, mainly in analogy with azo compounds, the structure of actual "arseno compounds" was assigned to them.

(II) $R-As=As-R$, $R = CH_3-$ arsenomethane [5];

$R = C_6H_5-$ arsenomethane [6].

However, a careful determination of the molecular weight by W. Steinkopf [7] led to the establishment of the following cyclic structure for arsenomethane:

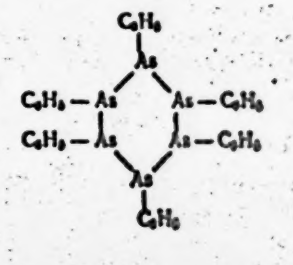
(III) 

These data were subsequently confirmed by other investigators [8]. Thus, there are no doubts about the structure of arsenomethane. The structure of arsenobenzene is a more complicated matter. Determination of the molecular weight of this compound by different investigators gave different results. Thus, for example, A Michaelis found 399.8 ebullioscopically in benzene [9] and S. Palmer found 402 under the same conditions and 642 cryoscopically in naphthalene [8]. An accurate determination of the molecular weight of arsenobenzene by F. Blicke and Smith [10] gave values of 895 and 915. It is apparently precisely this diversity which has led to the fact that up to the present time structural formula (II) has been accepted by all for arsenobenzene although it seems improbable that a compound of this structure would be colorless. We considered it extremely probable that the diversity of the results given above for the molecular weight of arsenobenzene is explained by the lability of the compound. Actually, even A. Michaelis [9] reported that arsenobenzene resinifies (polymerizes) very readily and according to our observations, these polymers (sticky, yellow resins) are exceptionally readily oxidized by atmospheric oxygen to C_6H_5AsO. Since arsenomethane is polymerized with more difficulty and its polymerization is readily observed as its polymers are completely insoluble in everything, the determination of its molecular weight gives accurate results. The resinification (polymerization) products of arsenobenzene are very readily soluble in benzene and other solvents, and likwise the oxidation products of the polymers, so that these reactions cannot be observed, and hence determination of the molecular weight of arsenobenzene gives unreliable data. All that has been presented convinced us that reliable data on the structure of arsenobenzene could only be obtained by x-ray structural analysis. We prepared arsenobenzene by reduction of C_6H_5AsO with hypophosphorous acid, and recrystallization of the product from toluene yielded almost colorless crystals with m.p. 210-212°, which agrees with literature data [10].

Crystals of arsenobenzene belong to the monoclinic system and appear as fine, yellowish needles. The long direction of the needles is the b axis; the simple forms are pinacoids {100} and {001}; the end faces were not developed. According to goniometric measurements, the monoclinic angle β was 110°09' ± 0°12'. Determination of the lattice constants from an oscillation x-ray diffraction pattern gave the following values: a = 11.93 ± 0.05 A; b = 6.11 ± 0.03 A; c = 23.57 ± 0.12 A. Hence the cell volume v = 1632 A^3 and with a density of 1.758 g/cc, this gives 11.3, i.e., 12 $C_6H_5-As=$ residues in a cell. Systematic extinctions showed that the space group was $C^5_{2h} = P2_1/c$, and consequently, the cell contained three crystallographically nonequivalent As atoms.

The structure was determined from the ac projection and the y coordinates were established by geometric analysis. The x and z coordinates of the As atoms, which were found first from the projection of the interatomic function, were used for determining the signs of F_{hol}. Then the electron density projection, showing the over-all contours of the benzene nuclei, was calculated. Unfortunately, due to their steep inclination to the projection plane, not all the carbon atoms were resolved on the plane; we had 10 maxima instead of 18 atoms. The second approximation of the electron density projection was derived with a reliability factor up to the value R = 14.5%, which left no doubt on the accuracy of the structure found.

As the electron density projection (Fig. 1) shows, the arsenobenzene molecule is a cyclic system of As atoms with one phenyl group attached to each. There are six members in the ring.

(IV) 

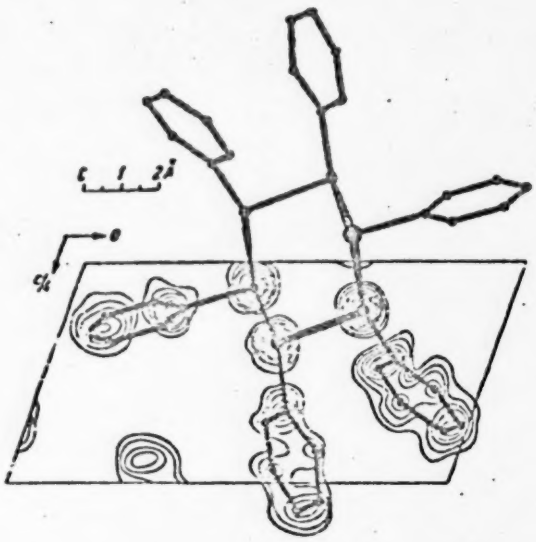


Fig. 1. Electron density projection of arsenobenzene on the ac face. The contour lines are in relative units.

These cyclic molecules are at the centers of symmetry in the crystal. The ring is not planar, but has a chair configuration with the As–As–As valence angle equal to 93 ± 2°. The outer As–As–C valence angles are 99 ± 3°. The bond length are as follows: As–As = 2.44 A; C–As = 1.96 A.

The data we obtained show that of all the data presented previously on the molecular weight of arsenobenzene, only those of F. Elicke and F. Smith [10] are accurate, while all the others are distorted by the reactions mentioned above. Since the results obtained by F. Elicke and F. Smith for arsenobenzene are accurate, the determinations of the molecular weights of p-arsenotoluene and p-arsenoanisole by these authors are also trustworthy. The values of 832 and 1080, and 1270, respectively, were found for the above compounds by these investigators. The values 996 and 1092 were calculated for the corresponding six-membered rings. Thus, one arrives at the conclusion that arseno compounds with the structure R–As = = As–R do not exist at all. They are actually either polymers, whose structure is illustrated by formulas (I) and (II), or cyclic compounds (III) and (IV). The whole story of arseno compounds again demonstrates the danger of assigning structures to compounds by analogy, as it was precisely by analogy that A. Michaelis assigned the structure $C_6H_5-As=As-C_6H_5$ to arsenobenzene [6] and that P. Ehrlich and A. Bertheim assigned the structure of 3,3'-diamino-4,4'-dihydroxyarsenobenzene to Salvarsan. In both cases the authors considered only elementary analysis data and the analogy with azo compounds.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

1,3-CYCLOPENTENEDIONE IN DIENE SYNTHESIS REACTIONS

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(Presented by Academician M. M. Shemyakin, December 19, 1959)

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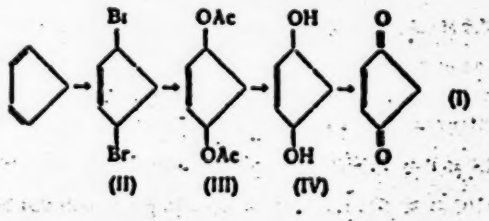
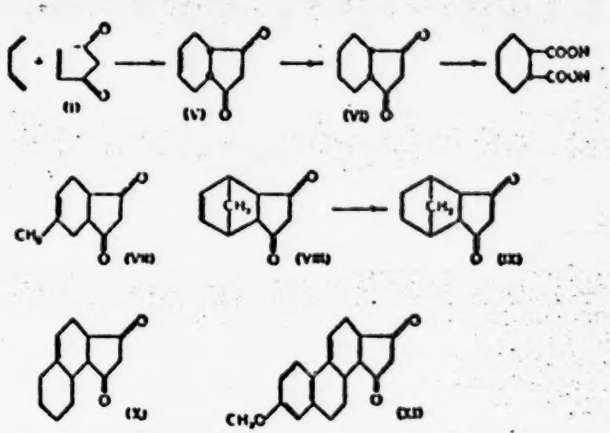
1,3-Cyclopentenedione (I), a brief communication on the preparation of which was published recently [1], is of undoubted interest for the synthesis and the study of the stereochemistry of polycyclic compounds, including those similar in nature. One of the possible ways of employing this unsaturated cyclic β-diketone synthetically is to use it as a dienophile in diene condensations with various dienes. Being a carbocyclic analog of maleic anhydride, this dienophile may be used successfully for constructing polycyclic systems, containing a five-membered ring with carbonyl groups in the α-position with respect to the coupling of the rings, which is extremely important both in the synthesis of compounds related to steroids and for studying the stereochemistry of hydrindanone systems.

The starting material for the preparation of 1,3-cyclopentenedione (I) is cyclopentadiene, which readily gives the dibromide (II), and conversion of the latter into the diacetate (III) and then into a mixture of isomeric cyclopentenediols (IV) has been described previously [2]. These diols are best oxidized to 1,3-cyclopentenedione by chromium trioxide in acetic acid and under these conditions, quite pure (m.p. 35-36°) diketone may be obtained in up to 30% yield.



1,3-Cyclopentenedione (I) readily undergoes a diene synthesis reaction with butadiene, even at room temperature, and gives a good yield of the corresponding cis-adduct (V), whose structure and configuration were demonstrated by oxidation of the corresponding 1,3-hydrindandione (VI) to the known cis-cyclohexane-1,2-dicarboxylic acid. The diketone condenses analogously with isoprene to form the adduct (VII) and also with cyclopentadiene to form the corresponding adduct (VIII), which added 1 mole to hydrogen when hydrogenated with a Pd catalyst and formed the corresponding endomethylene-1,3-hydrindandione (IX).

According to the infrared spectral data, the adducts obtained were completely enolized in solution and this is in agreement with results published recently [3].



1,3-Cyclopentenedione (I) readily condenses with 1-vinyl-Δ^3-cyclohexene and 6-methoxy-1-vinyl-$\Delta^{3,4}$-dihydronaphthalene to give good yields of the corresponding tri- and tetracyclic diketones (X) and (XI), of which the latter is of very great interest for further study of a structure related to steroid compounds. The ease and comparative similicity of the preparation of the adducts described has made them quite accessible for the study of various chemical conversions and this is the subject of our next work.

EXPERIMENTAL

Oxidation of 1,3-Cyclopentenediol (IV). Over a period of 15 minutes, a solution of 8.4 g of chromium trioxide in 100 ml of acetic acid was added to a solution of 6.3 g of 1,3-cyclopentenediol [2] (b.p. 107-108 at 0.7 mm, $n^{22}D$ 1.5025) in 50 ml of acetic acid cooled with ice water. The solvent was removed by distillation and to the residue was added 100 ml of 2 N H_2SO_4, the oxidation product extracted with benzene, the solvent removed, and the residue vacuum distilled. We obtained 1.5 g of cyclopentenedione-1,3 (I) with b.p. 60°/1 mm, $n^{22}D$ 1.5045, which crystallized immediately and had m.p. 35-36° [1]; the yield was 26%. The diketone (I) was obtained in 25% yield by oxidation of pure 1,3-cis-cyclopentenediol by the same procedure.

Found %: C 61.98; 61.92; H 4.56; 4.62 $C_5H_6O_2$. Calculated %: C 62.50; H 4.16

Condensation of 1,3-Cyclopentenedione (I) with Butadiene. A solution of 2.5 g of 1,3-cyclopentenedione (I) and 15 g of butadiene in 15 ml of benzene with a small amount of pyrogallol added was kept at room temperature for two weeks. The crystalline precipitate was collected by filtration to yield 2.46 g of adduct (V) which had m.p. 157.5-158.5° after recrystallization from absolute methanol.

Found %: C 71.90; 71.87; H 6.63; 6.71 $C_9H_{10}O_2$. Calculated %: C 71.98; H 6.71

1,3-Hydrindandione (VI) and Its Oxidation. A solution of 1.62 g of (V) in 50 ml of alcohol was hydrogenated over a Pd catalyst. Hydrogenation ceased after the absorption of 1 mole of hydrogen; the solvent was removed to yield 1.63 g of 1,3-hydrinandione (VI), which had m.p. 86-86.5° after recrystallization from absolute methanol.

Found %: C 70.73; 71.01; H 8.18; 7.97 $C_9H_{12}O_2$. Calculated %: C 71.02; H 7.95

For the oxidation, a cooled solution of 1 g of bromine in 17 ml of 10% NaOH was gradually added (over 15 minutes) to a cooled solution of 0.45 g of 1,3-hydrinandione (VI) in 3.5 ml of 10% NaOH. The mixture was stirred at 0° for 1 hour, the neutral products extracted with ether, and the alkaline solution saturated with SO_2 and evaporated in vacuum to half of its original volume. The precipitate was collected by filtration and extracted carefully with dry acetone. Removal of the acetone by distillation yielded 0.1 g of cis-cyclohexane-1,2-dicarboxylic acid with m.p. 186.5-187.5°, which did not depress the melting point of an authentic sample [3].

Condensation of 1,3-Cyclopentenedione (I) with Isoprene. A solution of 0.48 g of 1,3-cyclopentenedione (I) and 3.4 g of isoprene in 5 ml of benzene with a small amount of pyrogallol added was kept at room temperature in an ampoule for a month. The benzene was removed in vacuum and treatment of the residual oil with ether yielded 0.71 g of a crystalline reaction product with m.p. 83-87°, recrystallization of which from nitromethane gave pure adduct (VII) with m.p. 84.5-85.5°.

Found %: C 73.15; 72.89; H 7.49; 7.47 $C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.37

Condensation of 1,3-Cyclopentenedione (I) with Cyclopentadiene. To a solution of 0.24 g of 1,3-cyclopentenedione (I) in 3 ml of benzene was added 1.2 g of freshly distilled cyclopentadiene and the crystalline precipitate of reaction product collected by filtration. We obtained 0.40 g of adduct (VIII), which had m.p. 178-178.5° after recrystallization from absolute methanol.

Found %: C 74.10; 74.36; H 6.22, 6.16 $C_{10}H_{10}O_2$. Calculated %: C 74.05; H 6.22

A solution of 0.16 g of adduct (VIII) in 10 ml of absolute alcohol was hydrogenated over Pd catalyst. Hydrogenation ceased after the absorption of 1 mole of hydrogen; the solvent was removed by distillation to yield 0.15 g of endomethylene-1,3-hydrindandione (IX), which had m.p. 166-166.5° after recrystallization from absolute methanol.

Found %: C 73.46; 73.45; H 7.40; 7.22 $C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.37

Condensation of 1,3-Cyclopentenedione (I) with 1-Vinyl-Δ^3-cyclohexene. To a solution of 0.48 g of 1,3-cyclopentenedione (I) in 2.5 ml of benzene was added 1.62 g of 1-vinyl-Δ^3-cyclohexene [4] and the mixture kept at room temperature for a week. The benzene was removed and the thick dark oil treated with dry ether to yield 0.6 g of a crystalline product with m.p. 113-117°. After recrystallization from nitromethane, the pure adduct (X) had m.p. 120-121°.

Found %: C 76.20; 76.28; H 7.80; 7.75 $C_{13}H_{16}O_2$. Calculated %: C 76.44; H 7.90

Condensation of 1,3-Cyclopentenedione (I) with 6-Methoxy-1-vinyl-$\Delta^{3,4}$-dihydronaphthalene. To a solution of 0.46 g of 1,3-cyclopentenedione (I) in 2.5 ml of benzene was added a solution of 1 g of 6-methoxy-1-vinyl-$\Delta^{3,4}$-dihydronaphthalene [5] in 2.5 ml of benzene and the mixture left at room temperature for a day. We obtained 1 g of a crystalline reaction product with m.p. 205-207° (with decomp.). After crystallization from absolute methanol, adduct (XI) had m.p. 206.5-207.5°.

Found %: C 76.49; 76.32; H 6.63; 6.46 $C_{18}H_{18}O_3$. Calculated %: C 76.57; H 6.43

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REACTION OF AZODICARBOXYLIC ESTER WITH GEM-DIALKYLBUTADIENES

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(Presented by Academician A. N. Nesmeyanov, December 14, 1959)

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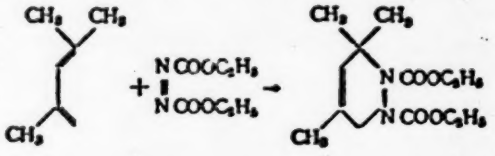
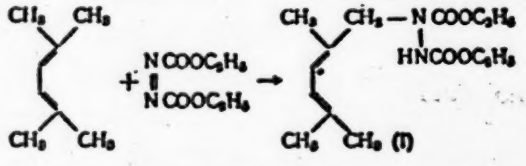
Original article submitted December 12, 1959

Continuing an investigation of the decomposition of alkyltetrahydropyridazines [1], we attempted to synthesize gem-dialkyltetrahydropyridazines from the adducts of azodicarboxylic ester and gem-dialkylbutadienes.

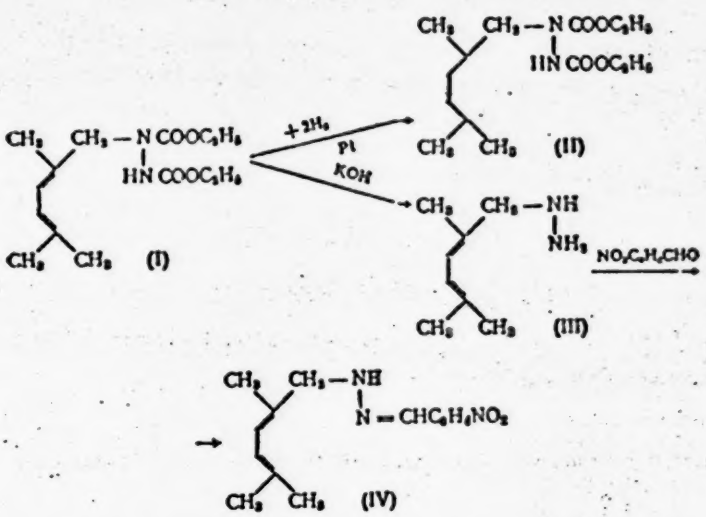
The reaction of axodicarboxylic ester with dienes of this structure was described by Diels et al. [2] and later by us [3]. As the gem-dialkylbutadienes, we used 2,4-dimethyl-1,3-pentadiene [2, 3], 2-methyl-2,4-hexadiene [3] and 2,5-dimethyl-2,4-hexadiene [3]. To the addition products we assigned the structure of 1,2-dicarbethoxy-Δ^4-tetrahydropyridazines – we considered that in this case the reaction proceeded according to the normal scheme for diene synthesis:



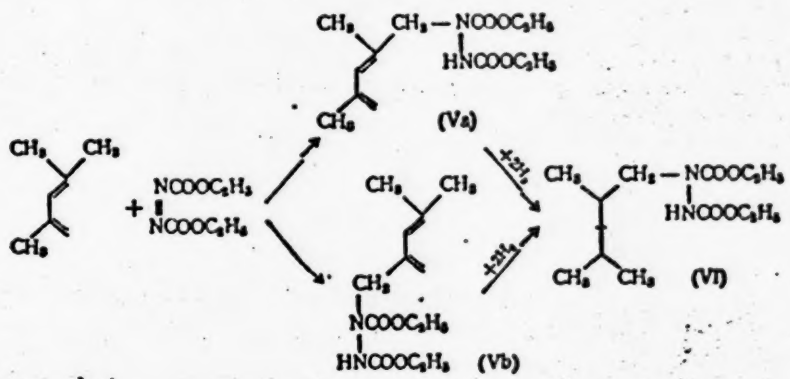
In the present work it was shown that the adducts of azodicarboxylic ester and gem-dialkylbutadienes actually have an acyclic structure (are not derivatives of tetrahydropyridazines), and are monosubstituted hydrazodicarboxylic esters, i.e., the reaction of gem-dialkylbutadienes with azodicarboxylic ester does not proceed according to a diene synthesis, but is a substitutive addition. Thus, for example, 2,4-dimethylpentadiene reacts with azodicarboxylic ester in the following way.



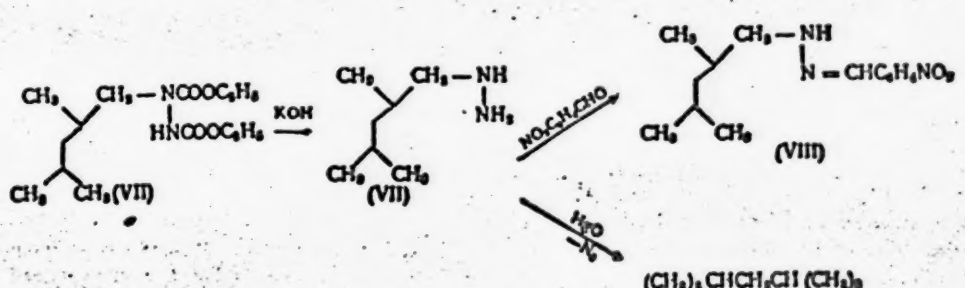
The structure of adduct (I) obtained was established by a study of some of its conversions. When hydrogenated in the cold it added 2 moles of hydrogen per mole of adduct and thus the molecule contained two double bonds. Hydrolysis of adduct (I) led not to 3,3,6,6-tetramethyl-Δ^4-tetrahydropyridazine (as should be the case had the addition proceeded according to the diene synthesis), but to the monosubstituted hydrazine (III). The presence of the NH_2 group in the latter was established by the preparation of the benzylidene derivative (IV) from it.



The reaction of azodicarboxylic ester with 2,4-dimethyl-1,3-pentadiene, which contains two types of methyl group, could form two addition products Va and Vb (in actual fact, a mixture of these compounds was apparently obtained). However, on hydrogenation they are both converted to the same substituted hydrazodicarboxylic ester (VI):

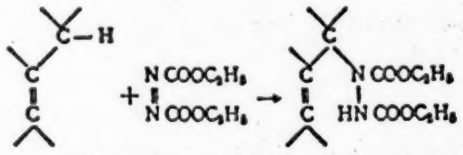


On hydrolysis, the latter formed a monosubstituted hydrazine (VII), which gave a benzylidene derivative (VIII) and also reacted with mercuric oxide to liberate nitrogen and form 2,4-dimethylpentane (this reaction is typical of monoalkylhydrazines [4]).



The reactions described quite definitely demonstrate the acyclic structure of the addition products of gem-dialkylbutadienes and azodicarboxylic ester. It is evident that the dienes we studied react with azodicarboxylic ester through one of their methyl groups.

The capacity of azodicarboxylic ester to undergo a substitutive addition with monoolefins has been described in the literature [5-8]. It was shown that the reaction occurs at the carbon atom in a position α to the double bond [6].



The substitutive addition of olefins to maleic anhydride, which has been studied in much more detail, also occurs at the α-position [8]. However, while maleic anhydride reacts in this way only at 200-250°, in the case of the more active azodicarboxylic ester, the reaction occurred at only 20-50°.

Thus, in the present work it was established for the first time that 1,1-dialkylbutadienes react with azodicarboxylic ester not through their double bonds, but through a labile hydrogen in the α-position (by a substitutive addition).

EXPERIMENTAL

Adducts of Gem-dialkylbutadienes and Azodicarboxylic Ester. To a solution of 0.2 mole of diene (2,4-dimethyl-1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene) in 50 ml of anhydrous benzene was added 35 ml of azodicarboxylic ester (heat was evolved) and the mixture left at room temperature for 5-7 hours. The benzene was then removed by distillation and the residue vacuum distilled in a stream of nitrogen. The adduct of 2,4-dimethyl-1,3-pentadiene (V) was apparently a mixture of two isomeric pentadienylhydrazodicarboxylic esters. The yield was 70-75% and the product had b.p. 172-175°/10 mm; $n^{20}D$ 1.4760; d^{20}_4 1.0637; MR 71.68; for $C_{13}H_{22}O_4N_2F_2$ calculated* 71.77.

Found %: C 57.54; 57.37; H 8.33; 8.15 $C_{13}H_{22}O_4N_2$. Calculated %: C 57.74; H 8.21

Literature data [2]: b.p. 136°/0.4-0.5 mm.

The Adduct of 2,5-Dimethyl-2,4-pentadiene (I; 2,5-dimethyl-2,4-hexadienyl-1-hydrazodicarboxylic ester) had b.p. 185-187/15 mm; $n^{20}D$ 1.4738; d^{20}_4 1.0390; MR_D 76.90; for $C_{14}H_{24}O_4N_2F_2$ calculated 76.39.

Found %: C 59.01; 58.98; H 8.50; 8.37 $C_{14}H_{24}O_4N_2$. Calculated %: C 59.13; H 8.51

Hydrogenation of Adducts. The adducts were hydrogenated in the cold (in a long-necked hydrogenation flask) in absolute alcohol (40% solution) in the presence of a platinum catalyst. After 8-12 hours, 1.85-1.95 moles of hydrogen had been absorbed per mole of adduct. The catalyst was removed by centrifuging, the alcohol evaporated, and the residue vacuum distilled in a stream of nitrogen.

2,4-Dimethylpentyl-1-hydrazodicarboxylic Ester (VI; from the adduct of 2,4-dimethyl-1,3-pentadiene) was obtained in 92% yield. It had b.p. 169-170°/10 mm, $n^{20}D$ 1.4530; d^{20}_4 1.0207; MR_D 72.64; for $C_{13}H_{26}O_4N_2$ calculated 72.70.

Found %: C 56.90; 56.82; H 9.50; 9.44 $C_{13}H_{26}O_4N_2$. Calculated %: C 56.91; H 9.55

2,5-Dimethylhexyl-1-hydrazodicarboxylic Ester (II; from the adduct of 2,5-dimethyl-2,4-hexadiene) was obtained in 90% yield. It had b.p. 175-176°/8 mm; $n^{20}D$ 1.4570; d^{20}_4 1.0120; MR_D 77.61; for $C_{14}H_{28}O_4N_2$ calculated 77.32.

Found %: C 58.41; 58.45; H 9.50; 9.44 $C_{14}H_{28}O_4N_2$. Calculated %: 58.31; H 9.56

* The atomic refraction of nitrogen was taken as 2.48 here and subsequently [8].

Hydrolysis of Hydrazodicarboxylic Esters. The adduct of 2,5-dimethylhexadiene and azodicarboxylic ester (I) and the hydrogenated adduct of 2,4-dimethyl-1,3-heptadiene (VI) were hydrolyzed.

To a solution of 0.1 mole of hydrazodicarboxylic ester in 40 ml of ethyl alcohol was added a solution of 29 g (0.5 mole) of potassium hydroxide in 50 ml of alcohol and the mixture heated for 3-4 hours on a water bath. The potassium carbonate precipitate was removed with suction and washed with ether; the solvent was distilled from the filtrate and the residue vacuum distilled in a stream of nitrogen.

2,5-Dimethyl-2,4-hexadienyl-1-hydrazine (III); from the adduct of 2,5-dimethyl-2,4-hexadiene) was obtained as a viscous oil, which distilled with decomposition, was unstable in air, and had b.p. 88-90°/20 mm. The p-nitrobenzylidene derivative (IV) had m.p. 303° (from acetic acid).

Found %: C 66.00; 65.83; H 7.03; 6.88 $C_{15}H_{19}O_2N_3$. Calculated %: C 65.91; H 7.01

2,4-Dimethylpentyl-1-hydrazine (VII; from the hydrogenated adduct of 2,4-dimethyl-1,3-pentadiene) had b.p. 84-85°/25 mm; $n^{20}D$ 1.4550; d^{20}_4 0.8533; MR_D 41.40; for $C_7H_{18}N_2$ calculated 41.68.

Found %: C 65.30; 65.36; H 12.60; 12.60; N 21.91; 21.87 $C_7H_{18}N_2$. Calculated %: 65.60; H 12.60; N 21.80

The p-nitrobenzylidene derivative (VIII) had m.p. 112-113° (from acetic acid).

Found %: C 63.70; 63.65; H 8.01; 7.87 $C_{14}H_{21}O_2N_3$. Calculated %: C 63.85; H 8.04

Oxidation of 2,4-Dimethylpentyl-1-hydrazine. With vigorous stirring, 32.5 g (0.15 mole) of yellow mercuric oxide was gradually added to a solution of 13 g (0.1 mole) of 2,4-dimethylpentylhydrazine in 50 ml of ether. There was evolution of heat and vigorous evolution of gas (2.0 liters, 98% N_2). When the reaction was complete, the ether solution was decanted from the precipitate of metallic mercury and excess mercuric oxide and dried with calcium chloride, the ether distilled with a tall fractionating column, and the residue distilled to yield the 2,4-dimethylpentane formed (72% yield). The product had b.p. 79-80°/752 mm; $n^{20}D$ 1.3830; d^{20}_4 0.6745. Literature data [9]: b.p. 80.7°/760 mm; $n^{20}D$ 1.3821; d^{20}_4 0.6738.

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STRUCTURE OF SOME CYCLIC 2-NITRO-1,3-DIKETONES

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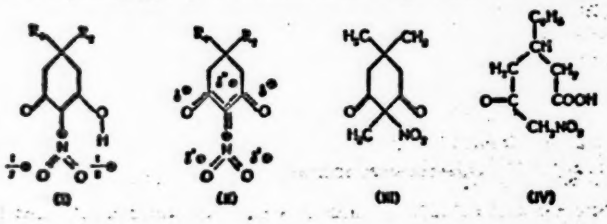
In continuing our investigations of tautomerism in cyclic 2-nitro-1,3-diketones [1, 2], we studied 2-nitrodimedone (I, $R_1 = R_2 = CH_3$), 2-nitro-5-phenylcyclohexane-1,3-dione (2-nitrophendione; I, $R_1 = H$, $R_2 = C_6H_5$), and their anions and some related compounds. During the investigations we determined the structure of these compounds and also the difference between the three nitration products of phendione: a compound with m.p. 120-121°, obtained by recrystallization from benzene, a compound with m.p. 131-132°, obtained by precipitation from saturated aqueous solution with hydrochloric acid [3], and a compound with m.p. 119-120°, obtained by recrystallization from aqueous solutions, but corresponding in elementary composition to a product with one molecule of water.

Infrared spectra were plotted for the substances in the solid state (suspensions in paraffin oil) and in chloroform solutions; the ultraviolet spectra were plotted for 10^{-4} M solutions of the compounds in H_2O, CH_3OH, or $CHCl_3$. Polarograms were plotted for 10^{-4} M aqueous solutions of the substance in Britton and Robinson's buffer solutions with a base electrolyte of 0.1 N KCl. The experimental data are summarized in the table. The infrared spectra show that 2-nitrodimedone and 2-nitrophendione have the same structure in chloroform, namely, the form of a nitro enol, where the hydroxyl group is involved in a strong intramolecular hydrogen bond.



(I) (II) (III) (IV)

Of the separate absorption frequencies, the frequency at ~1540 cm^{-1} should be ascribed to oscillations of the nitro group, the frequency at ~1570 cm^{-1} to oscillations of the C—C bond, reduced in comparison with the enol ether of dimedone, and the frequency at 1690 cm^{-1} to oscillations of the carbonyl group, increased in comparison with the oscillations of a normal conjugated carbonyl. The latter is explained by some change in the multiplicity of the C = C bond due to the formation of a strong intramolecular ring, which is the reason for the decrease in the conjugation of the carbonyl and the double bond.

That the molecules of 2-nitrodimedone and 2-nitrophendione have identical structures in chloroform solutions is also confirmed by the similarity of their ultraviolet absorption spectra. Within the range 2370-3500 A, both compounds have an absorption band at 2930 (2960) A, caused by the chromophoric grouping $OH\text{-}\overset{|}{C} = \overset{|}{C}\text{-}NO_2$ but not the absorption maximum for the grouping $>C=\overset{|}{C}-\overset{|}{C}=O$ due to the strong absorption in chloroform. In the case of 2-nitrodimedone, the infrared absorption spectrum of the solid substance differs noticeably

Compound	Infrared absorption in cm^{-1} (percent absorption in brackets)		Ultraviolet absorption in A ($\epsilon \cdot 10^4$ in brackets)			Levels of polarographic wave $E_{1/2}$ in v
	solid	$CHCl_3$	H_2O	CH_3OH	$CHCl_3$	
2-Nitrodimedone*	1523 (100); 1625 (94); 1661 (83)	1547 (93); 1564 (95); 1680 (88)	2620 (1.50)*; 3330 (1.31)	—	2960 (0.70)	
2-Nitrophendione (m.p. 131-132°)	1525 (84); 1559 (93); 1682 (88)	1542 (89); 1567 (90); 1689 (86)	—	—	2990 (0.53)	
2-Nitrophendione (m.p. 120-121°)	1523 (88); 1556 (97); 1682 (88)	—	2610 (1.46); 3330 (0.34)	—	—	
NH_4 salt of 2-nitrodimendone (m.p. 190-192°)	1568 (90); 1625 (68)	—	—	2650 (1.73)	—	—1.16—0.080 pH
NH_4 salt of 2-nitrophendione (m.p. 197-198°)	1577 (92); 1612 infl.	—	—	2640 (1.69)	—	—0.11—0.000 pH
2-Nitro-2-methyldimedone	1560 (98); 1715 (97); 1748 (87)	—	—	—	—	—
2,2-Dimethyldimedone	1694 (46); 1724 (46)	1702; 1730 [6]				
Ethyl ether of dimedone	1613 (93); 1669 (69)	1605 (90) 1645 (68) [14]	—	2500 (1.92)	—	
6-Nitro-3-phenyl-5-hexanonoic acid (m.p. 119-120°)	1560 (100); 1695 (100); 1728 (85)	—	2350 (infl.)** 33 0 (0.39) 2320 (0.29) 0.1 N 3250 (1.16) KOH	—	—	—0.12—0.076 pH*** —0.69—0.68 pH

* Potassium salt in aqueous solution ~2610 A (1.52) and ~3400 A (0.29) [13].

** When the solution stood, ϵ fell rapidly (to 0.11 in a day).

*** The wave fell rapidly when the solution stood.

from the spectrum of the chloroform solution. The spectrum shows that 2-nitrodimedone also exists in the nitro enol form in the solid state, but in this case intermolecular rather than intramolecular interaction of the groups predominates.

On the other hand, the infrared spectra of solid 2-nitrophendione indicate firstly that the two modifications with different melting points (131-132° and 120-121°) have the same structure and, secondly, that the structure is close to the state of the molecule in $CHCl_3$ solution, i.e., is a nitro enol with an intramolecular hydrogen bond, though there may also be intermolecular interaction to some extent. The difference between 2-nitrophendione and 2-nitrodimedone in the solid state may be explained by crystallochemical factors and also hindrance to intermolecular interaction with 2-nitrophendione due to the presence of the large phenyl radical. In the region of 2400-4000 cm^{-1}, nothing could be detected apart from oscillations of the C—H bond in the case of both compounds investigated; it is possible that C—H and O—H oscillations overlapped.

The third modification of 2-nitrophendione with m.p. 119-120°, which we first thought to be identical with the modification with m.p. 120-121°, has a completely different structure. However, the strong depression of a mixed melting point, the presence of an additional molecule of water in the molecular composition, the lack of color in alkaline solutions, and spectroscopic and polarographic data convinced us that the formation of a "hydrate" involved opening of the six-membered ring and that the substance was 6-nitro-3-phenyl-5-hexanonoic acid (IV). This was demonstrated by its infrared spectrum, where the frequency at 1560 cm^{-1} corresponds to higher oscillations of the nitro group (due to the effect of the neighboring carbonyl), the frequency at 1695 cm^{-1} to the carbonyl group, and the frequency at 1728 cm^{-1} to high oscillations of the carbonyl, due to the effect of the nitro group. As an α-nitro ketone, compound (IV) rapidly decomposes in aqueous solutions [4] to give nitromethane and β-phenylglutaric acid, which is demonstrated by infrared spectra and polarograms of the solutions. When the solution was stored, the maximum at 3300 A fell rapidly and all absorption in the near ultraviolet had disappeared after a week. Freshly prepared solutions of the substance gave a polarographic wave with $E_{1/2} = -0.49$ v (pH 5), which fell rapidly and a new wave with $E_{1/2} = -0.84$ v (pH 5) appeared; the latter may be ascribed to nitromethane [5].

Consequently, when 2-nitrophendione is boiled in aqueous solutions, the ring is opened readily with the formation of 6-nitro-3-phenyl-5-hexanonoic acid, which is unstable in aqueous solutions.

The infrared spectra of solid ammonium salts of 2-nitrodimedone and 2-nitrophendione indicated the existence of the mesomeric anion (II), where the charge is distributed between the two carbonyl and the nitro groups. The proportions of the charges δ, δ', and δ'', localized on separate centers, are difficult to evaluate as yet, but it can be assumed that in the given systems the electron density on the carbonyl groups is strongly decreased, as is indicated by the hypsochromic displacement of the K band in the ultraviolet spectra in comparison with the unsubstituted enolate anion [6] and the displacement of the characteristic frequencies of the enolate anion (1500-1520 cm^{-1}) [7] toward higher values in the infrared spectra. At the same time, on comparing the displacements of the maxima of the infrared and ultraviolet absorption spectra of the anions of 1,3-cyclohexanediones and their nitro derivatives on the one hand, and of 1,3-indandione [8] and 2-nitro-1,3-indandione [ultraviolet absorption maxima, in aqueous solutions, of 2270 A (1.83), 2410 (1.56 infl.), 3030 (1.16) and 3470 (1.87)] on the other, it seems probable that the distribution of electron density in mesomeric 2-nitro enolate anions is different and in the case of anions of 2-nitro-1,3-cyclohexanediones the distribution corresponds more to the enolate anion rather than the aci-nitro form, which is the case in 2-nitro-1,3-indandione [2].

2-Nitro-2-methyldimedone (III) was chosen as a model substance of the nitro diketo form; in this case the frequency at 1560 cm^{-1} was ascribed to oscillations of the nitro group and the frequencies at 1715 cm^{-1} to oscillations of the carbonyl groups. A comparison of 2-nitro-2-methyldimedone with 2,2-dimethyldimedone shows that the frequencies of the carbonyl groups in α-nitro ketones are high in comparison with the normal carbonyl frequency; in their turn, the frequencies of the nitro group here are also increased (from 1540 to 1560 cm^{-1}). A similar effect of the interaction of a nitro group with an α-carbonyl on the infrared spectrum is also demonstrated by some literature data [9, 10].

A comparison of 2-nitrodimedone and 2-nitrophendione with 2-nitro-1,3-indandione [2] leads to the conclusion that these compounds differ fundamentally in structure. While the first two are nitro enols in the solid state, the last exists in the form of a nitro diketone or an ionized nitronic acid. While anions of 2-nitrodimendone and 2-nitrophendione salts are apparently close to the structure of an enolate anion, the anion of 2-nitro-1,3-indandione corresponds almost completely to the structure of the anion of the aci-nitro form. Potentiometric measurements showed that in aqueous solutions, 2-nitrodimedone and 2-nitrophendione are acids with dissociation constants of the order of 10^{-3}, i.e., are approximately equal in strength to formic acid, while 2-nitro-1,3-indandione is a strong acid which is completely dissociated at all concentrations.

Some confirmation of the difference in structure between the anions of 2-nitrodimedone (2-nitrophendione) and 2-nitro-1,3-indandione is also given by their polarographic behavior, as the "nitro group" in the first two anions is reduced somewhat more readily than the "nitro group" in 2-nitroindandionate, despite conjugation with the aromatic ring in the molecule of the latter, which makes it much easier to reduce the carbonyl in 2-nitroindandionate than in 2-nitrodimedonate and 2-nitrophendionate [11].

The differences in structure presented above may be explained if it is assumed that 2-nitrodimedone and 2-nitrophendione have a stable six-membered ring, while the molecule of 2-nitro-1,3-indandione contains a more strained five-membered ring, where the endocyclic double bonds are less favored than exocyclic ones [2]. Therefore, in the case of 2-nitro-1,3-indandione there is a tendency for the formation of the keto nitronic acid, while in the case of the alicyclic six-membered nitro β-diketones, the formation of the nitro enol is possible.

The ultraviolet spectra were plotted by A. Grinvalde and M. Tiltin.

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1-(1'-HALOFERROCENYL)-BORIC ACIDS IN THE SYNTHESIS OF FERROCENE DERIVATIVES

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As we described previously, ferrocenylboric and 1,1'-ferrocenylenediboric acids [1] may be used for the synthesis of various ferrocene derivatives. 1,1'-Ferrocenylenediboric acid was used to prepare disubstituted ferrocene derivatives with identical substituents in the cyclopentadienyl rings. The replacement of only one $B(OH)_2$ group by halogen leads to 1-(1'-haloferrocenyl)-boric acids, which are interesting as starting materials for the synthesis of some ferrocene derivatives with different substituents in the two cyclopentadienyl rings.

In the present work it was shown that the reaction of 1,1'-ferrocenylenediboric acid in a benzene–water mixture with cupric chloride or bromide, in an amount equivalent to one $B(OH)_2$ group, forms 1-(1'-chloroferrocenyl)- and 1-(1'-bromoferrocenyl)-boric acids.

$$(HO)_2BC_5H_4FeC_5H_4B(OH)_2 \xrightarrow{CuX_2} XC_5H_4FeC_5H_4B(OH)_2,$$

where X is Cl or Br.

The structure of 1-(1'-haloferrocenyl)-boric acids was confirmed by the formation of the corresponding haloferrocenes when they were hydrolyzed in the presence of zinc salts.

1-(1'-Haloferrocenyl)-boric acids reacted like arylboric acids with mercury salts to form the corresponding mercury compounds of ferrocene, 1-(1'-chloroferrocenyl)-mercuric chloride and 1-(1'-bromoferrocenyl)-mercuric bromide, which were readily symmetrized by sodium thiosulfate to di-1-(1'-chloroferrocenyl)-mercury and di-1-(1'-bromoferrocenyl)-mercury. By the action of iodine on these organomercury compounds of ferrocene, according to the procedure described for ferrocenylmercuric chloride [2], we obtained the previously unknown 1'-chloro-1-iodoferrocene and 1'-bromo-1-iodoferrocene.

In an attempt to prepare heteroannular chlorobromoferrocene by the action of cupric chloride on 1-(1'-bromoferrocenyl)-boric acid, we isolated 1,1'-dichloroferrocene.

$$BrC_5H_4FeC_5H_4B(OH)_2 \xrightarrow{CuCl_2} ClC_5H_4FeC_5H_4Cl.$$

This reaction confirmed the case of replacement of a halogen in the ferrocene nucleus in the presence of copper salts, which we found previously [3].

EXPERIMENTAL

1-(1'-Chloroferrocenyl)-boric Acid. Into a flask with a stirrer and a reflux condenser was placed 3.1 g of 1,1'-ferrocenylenediboric acid, moistened with 7 ml of methanol, and 4.7 g of $CuCl_2 \cdot 2H_2O$ (20% excess) in 75 ml

of water and 60 ml of benzene added. The mixture was boiled for 2.5 hr, then cooled, and the unreacted 1,1'-ferrocenylenediboric acid removed by filtration. The benzene layer was separated and the aqueous layer used for a repeat of the operation with the unreacted 1,1'-ferrocenylenediboric acid, with the addition of 70 ml of benzene. The aqueous layer was then separated from the benzene again, saturated with NaCl, and extracted with ether. The benzene and ether extracts were combined and evaporated to 50 ml. The 1-(1'-chloroferrocenyl)-boric acid was extracted with 10% KOH solution and the alkaline solution washed twice with ether and acidified with 10% H_2SO_4. The precipitated 1-(1'-chloroferrocenyl)-boric acid was collected by filtration, washed with water, and dried over 65% H_2SO_4. The yield of 1-(1'-chloroferrocenyl)-boric acid was 1.56 g (52% of theoretical). The acid was sufficiently pure for further work. It was recrystallized from water or aqueous alcohol, but did not have a sharp melting point; it had m.p. 159-161° (when introduced in a capillary into a previously heated apparatus).

Found %: C 45.53; 45.40; H 3.72; 3.77; Cl 13.76; 13.49; Fe 20.76; 20.85; B 4.02; 4.04 $C_{10}H_{10}ClFeBO_2$. Calculated %: C 45.45; H 3.81; Cl 13.42; Fe 21.13; B 4.09

1-(1'-Bromoferrocenyl)-boric Acid. Similarly, from 4 g of 1,1'-ferrocenylenediboric acid, 6 ml of methanol, 8 g of $CuBr_2$ in 120 ml of water, and 100 ml of benzene we obtained 2.9 g of 1-(1'-bromoferrocenyl)-boric acid (65% of theoretical). The substance was recrystallized from water or aqueous alcohol. In the melting point determination, the substance softened at 130°, solidified again, and melted at 155-157°.

Found %: C 38.85; 39.03; H 3.22; 3.37; B 3.50; Br 25.42; Fe 18.05 $C_{10}H_{10}BrFeBO_2$. Calculated %: C 38.89; H 3.26; B 3.50; Br 25.88; Fe 18.09

Hydrolysis of 1-(1'-Haloferrocenyl)-boric Acids. To 0.16 g of 1-(1'-chloroferrocenyl)-boric acid in 50 ml of water was added 0.25 g of $ZnCl_2$. The mixture was steam distilled to give chloroferrocene, which was extracted with ether and the ether evaporated from the extract. We obtained 0.10 g of chloroferrocene (79% of theoretical) with m.p. 52-54°, which rose to 57-58° when the substance was recrystallized from alcohol; a mixed melting point with authentic chloroferrocene was not depressed.

Similarly, by hydrolysis of 0.20 g of 1-(1'-bromoferrocenyl)-boric acid, in the presence of 0.4 g of zinc bromide, in 40 ml of water we obtained 0.15 g of bromoferrocene (88% of theoretical) with m.p. 28.5-30.5°, which rose to 32-33° when the substance was recrystallized from methanol; a mixed melting point with authentic bromoferrocene was not depressed.

1-(1'-Chloroferrocenyl)-mercuric Chloride. To a hot solution of 0.27 g of 1-(1'-chloroferrocenyl)-boric acid in 5 ml of alcohol with 50 ml of water was added an aqueous acetone solution of 0.28 g of mercuric chloride. A yellow precipitate formed. The mixture was heated for a further 5 minutes and then the precipitate collected, washed with water, and dried in vacuum over P_2O_5. We obtained 0.41 g (88% of theoretical) of 1-(1'-chloroferrocenyl)-mercuric chloride with m.p. 141-143°, which rose to 144.5-145° when the substance was recrystallized from acetone.

Found %: C 26.48; 26.55; H 1.78; 1.92; Cl 15.58; 15.49; Hg 43.41; 43.54; Fe 12.33; 12.38 $C_{10}H_8Cl_2HgFe$. Calculated %: C 26.36; H 1.77; Cl 15.57; H 44.04; Fe 12.26

1-(1'-Bromoferrocenyl)-mercuric Bromide. Similarly, from 0.30 g of 1-(1'-bromoferrocenyl)-boric acid and 0.36 g of $HgBr_2$ we obtained 0.46 g of 1-(1'-bromoferrocenyl)-mercuric bromide (84% of the theoretical) with m.p. 142.5-145°, which rose to 146.5-147° when the substance was recrystallized from acetone.

Found %: C 22.17; 22.15; H 1.41; 1.48; Br 29.20; 29.15; Hg 36.21; 36.37; Fe 10.39; 10.62 $C_{10}H_8Br_2HgFe$. Calculated %: C 22.06; H 1.48; Br 29.35; Hg 36.84; Fe 10.26

These mercury compounds were yellow crystalline substances, which were soluble in acetone, benzene, and chloroform and more difficultly soluble in ether and alcohol.

Di-1-(1'-chloroferrocenyl)-mercury. 1-(1'-Chloroferrocenyl)-mercuric chloride (0.33 g), moistened with acetone, in 20 ml of 50% sodium thiosulfate solution was shaken for several hours. The di-1-(1'-chloroferrocenyl)-mercury was then collected by filtration, washed with water, and dried over P_2O_5. The yield was 0.21 g (85% of theoretical) and the m.p. 146-147°, which rose to 151-152° when the substance was recrystallized from a mixture of xylene and hexane (with rapid cooling of the solution).

Found %: C 37.57; 37.56; H 2.63; 2.60; Cl 11.08; 11.20; Hg 31.00; 31.03; Fe 17.84; 17.92 $C_{20}H_{16}Cl_2Hg_2Fe_2$. Calculated %: C 37.55; H 2.52; Cl 11.09; Hg 31.38 Fe 17.47

Di-1-(1'-bromoferrocenyl)-mercury. Similarly, from 0.35 g of 1-(1'-bromoferrocenyl)-mercuric bromide in 20 ml of 50% sodium thiosulfate solution we obtained 0.245 g (94% of theoretical) of di-1-(1'-bromoferrocenyl)-mercury with m.p. 134-135°. After recrystallization from nitromethane, the substance had m.p. 135-136°.

Found %: C 32.93; 33.28; H 2.04; 2.10; Br 21.69; 21.83; Hg 27.23; 27.34; Fe 15.13; 15.45 $C_{22}H_{18}Br_2HgFe_2$. Calculated %: C 32.97; H 2.24; Br 21.94; Hg 27.54; Fe 15.33

The symmetrical 1-(1'-haloferrocenyl)-mercury compounds partly decomposed when heated in xylene or nitromethane solutions. Thus, bromoferrocene was isolated after di-1-(1'-bromoferrocenyl)-mercury had been heated in xylene and therefore these substances were recrystallized with high losses.

1'-Chloro-1-iodoferrocene. To a solution of 1.00 g of 1-(1'-chloroferrocenyl)-mercuric chloride in 10 ml of hot xylene was added a solution of 3 g of iodine in 10 ml of xylene. After the mixture had cooled, the black precipitate was collected by filtration, washed with alcohol, and shaken in a separating funnel with a solution of 45 g of sodium thiosulfate in 200 ml of water and ether. The yellow ether solution was filtered and the ether evaporated to yield 0.49 g of 1'-chloro-1-iodoferrocene (64% of theoretical) with m.p. 38-40°. A saturated solution of it in methanol at 40° was cooled with a mixture of dry ice and acetone to give yellow crystals with m.p. 42-44°.

Found %: C 34.63; 34.83; H 2.27; 2.35; Fe 16.28; 16.44; total halogens 47.19; 47.24 $C_{10}H_8ClIFe$. Calculated %: C 34.67; H 2.33; Fe 16.12; total halogens 46.87.

1'-Chloro-1-iodoferrocene was readily soluble in organic solvents.

1'-Bromo-1-iodoferrocene. Similarly, from 0.80 g of 1-(1'-bromoferrocenyl)-mercuric bromide in 10 ml of xylene and 3 g of iodine in 10 ml of xylene we obtained 0.44 g (76% of theoretical) of 1'-bromo-1-iodoferrocene with m.p. 25-26°; cooling a saturated methanol solution of 1'-bromo-1-iodoferrocene with a mixture of dry ice and acetone yielded yellow crystals with m.p. 28-30°.

Found %: C 30.62; 30.53; H 2.21; 2.22; Fe 13.87; 14.13 $C_{10}H_8BrIFe$. Calculated %: C 30.73; H 2.06; Fe 14.19

1'-Bromo-1-iodoferrocene was readily soluble in organic solvents.

Action of Cupric Chloride on 1-(1'-Bromoferrocenyl)-boric Acid. 1,1'-Dichloroferrocene. A mixture of 1 g of 1-(1'-bromoferrocenyl)-boric acid and 1.7 g of cupric chloride in 120 ml of water was placed in a steam-distillation flask. After steam distillation, the 1,1'-dichloroferrocene was extracted with ether and the ether evaporated from the extract. We obtained 0.60 g of 1,1'-dichloroferrocene with m.p. 72-74°, which rose to 75-77° when the substance was recrystallized from alcohol; a mixed melting point with an authentic sample was not depressed and the C and H analyses corresponded to dichloroferrocene.

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KINETICS OF HYDRODESULFURIZATION REACTIONS

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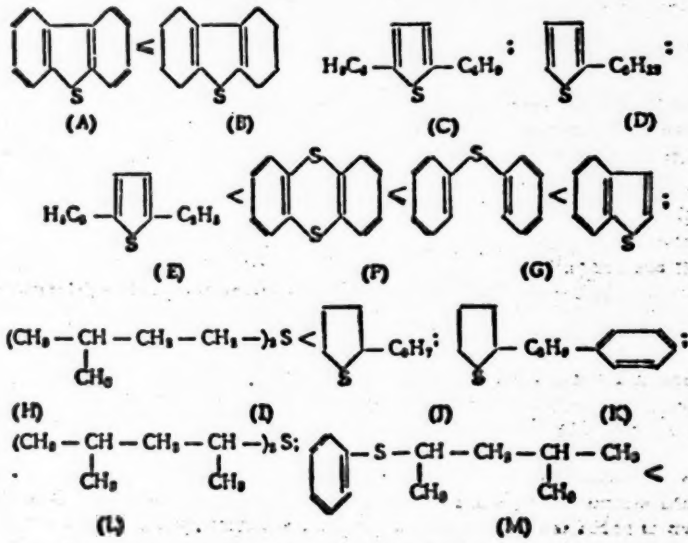
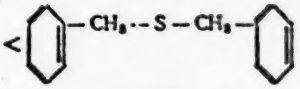
The information in the literature on the kinetics of hydrodesulfurization reactions of organosulfur compounds, which are important in technology, is limited to data on thiophene, dibenzothiophene, and octahydrodibenzothiophene [1-4].

In the present work the results of a systematic study of the kinetics of hydrogenolysis of a series of sulfides and thiophenes in the presence of an aluminum-cobalt-molybdenum catalyst. The experimental procedure, analysis methods, and kinetic treatment adopted in our laboratory have been described previously [4]. As an example, Fig. 1 gives curves for the relation between the degree of conversion and the conventional contact time for 2,4,6,8-tetramethyl-5-thianonane. The nature of these curves is typical of all the organosulfur compounds we studied.

The hydrogenolysis was described well by the equation proposed in a general form by Frost and Kazeev. The parameters of these equations which we found are given in Table 1. An examination of these parameters shows that organosulfur compounds may be arranged in the following series in order of increasing rates of hydrogenolysis:





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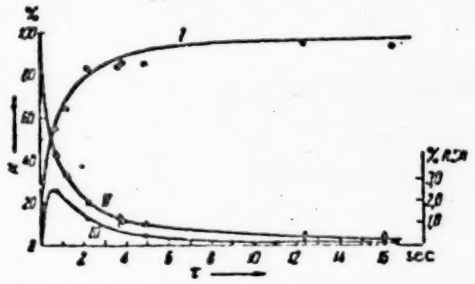


Fig. 1. Kinetics of hydrogenolysis of 2,4,6,8-tetramethyl-5-thianonane at T = 375°, P_{tot} = 40 atm, and P_{H_2} = 33.3 atm. I) Hydrogen sulfide sulfur; II) sulfide sulfur; III) mercaptan sulfur.

The values of the parameter α, which are proportional to the rate constants of hydrogenolysis of these compounds at 375° C that are of practical interest, are in the following ratios:

(A, B, C, D, E):(F, G):(H, I):(J, K, L, M):
:N = 1:2:3:4:7

This relation gives a theoretical basis to the possibility of the selective hydrodesulfurization of petroleum products on an aluminum–cobalt–molybdenum catalyst and also the use of this catalyst in the group analysis of organosulfur compounds. In addition, it gives a quantitative measure of the possibility of preferential rupture of the bond of a sulfur atom with carbon atoms, which makes it possible to predict the nature of the products formed by hydrogenolysis.

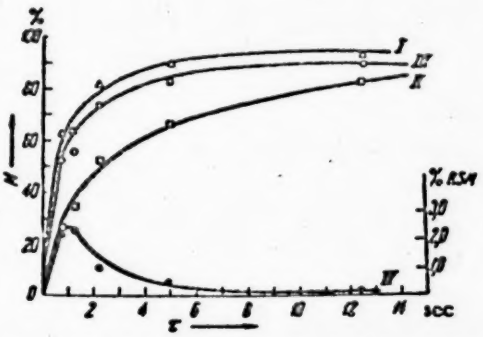


Fig. 2. Kinetics of the hydrogenolysis of a mixture of α-propyl-thiophane (0.51%), α-hexylthiophane (0.46%), 2,4,6,8-tetramethyl-5-thianonane (0.46%), 1,3-dimethyl-1-(phenylthio)-butane (0.46%), and dibenzothiophene (0.81%), dissolved in cetane, at T = 375°, P_{tot} = 40 atm, and P_{H_2} = 33.3 atm. I) Calculated kinetic curves for hydrogenolysis of the mixture of sulfides; II) the same for the hydrogenolysis of dibenzothiophene; III) the same for hydrogenolysis of the mixtures of sulfides and dibenzothiophene; IV) yield of mercaptan sulfur.

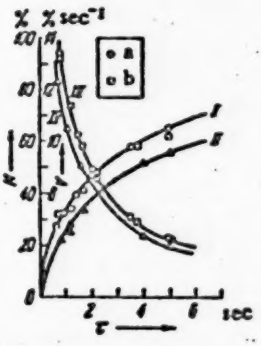


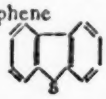
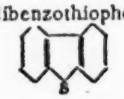
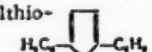
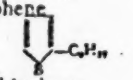
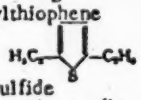
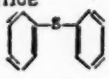
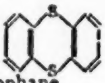
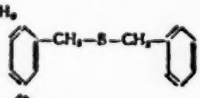
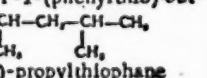
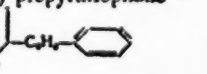
Fig. 3. Calculated relations for the extent of hydrogenolysis: I) dibenzothiophene (a); the same with hydrogen sulfide added (b); II) the same with biphenyl added; III) and IV) hydrogenolysis rates corresponding to I and II.

The rate of hydrogenolysis of a mixture of organosulfur compounds was found to obey the additivity rule, as is confirmed by the curves in Fig. 2. This makes it possible to predict the change in composition of organosulfur compounds during the hydrofining of petroleum products.

To study the effect of reaction products on the hydrogenolysis rate, we carried out experiments on the hydrogenolysis of dibenzothiophene, unsolved in cetane with biphenyl and hydrogen sulfide added. It was shown that the limiting extent and the rate of hydrogenolysis fell sharply when biphenyl was added to the starting solution of

TABLE 1

Parameters of Frost and Kazeev's Equations*

Compound	Temp. °C	P_{H_2}, atm.	β	n	a	b	D
Dibenzothiophene 	325	33.3	1.0	0.62	0.31	0.69	78
	375	9.4	1.0	0.32	0.10	0.68	70
	375	19.9	1.0	1.14	0.23	0.65	79
	375	33.5	1.0	1.34	0.44	0.65	91
	375	36.5	1.0	1.05	0.50	0.64	94
	425	33.3	1.0	2.29	0.61	0.62	95
	$E_{app.}$=10.8 kcal/mole				E=6.6 kcal/mole		
Octahydrodibenzothiophene 	325	33.3	1.0	0.94	0.32	0.70	83
	375	9.5	1.1	0.51	0.14	0.71	68
	375	20.0	1.0	1.46	0.28	0.71	78
	375	33.5	1.0	1.77	0.52	0.72	90
	375	37.0	1.0	0.86	0.55	0.71	93
	425	33.3	1.0	2.73	0.71	0.58	95
	$E_{app.}$=8.9 kcal/mole				E=6.1 kcal/mole		
2,5-Dibutylthiophene 	325	33.3	1.0	1.0	0.40	0.65	85
	375	33.3	1.0	1.7	0.53	0.65	90
	425	33.3	1.0	2.5	0.71	0.68	95
	$E_{app.}$=7.6 kcal/mole				E=4.8 kcal/mole		
2-Octylthiophene 	325	33.3	1.0	0.96	0.30	0.70	89
	375	33.3	1.0	1.7	0.46	0.69	92
	425	33.3	1.0	3.0	0.70	0.71	95
	$E_{app.}$=9.8 kcal/mole				E=6.9 kcal/mole		
2,5-Diethylthiophene 	375	33.3	1.0	1.8	0.56	0.66	90
Diphenyl sulfide 	325	33.3	1.0	1.62	0.45	0.65	93
	375	15.0	1.0	2.29	0.25	0.68	92
	375	20.0	1.0	3.69	0.38	0.68	93
	375	33.3	1.0	3.25	0.73	0.66	94
	375	38.0	1.0	1.52	0.93	0.66	95
	425	33.3	1.0	4.65	0.95	0.64	95
	$E_{app.}$=8.6 kcal/mole				E=5.4 kcal/mole		
Thianthrene 	325	33.3	1.0	1.22	0.38	0.73	91
	375	33.3	1.0	2.27	0.54	0.73	94
	425	33.3	1.0	3.16	0.69	0.73	95
	$E_{app.}$=8.3 kcal/mole				E=4.9 kcal/mole		
α-Propylthiophane	325	33.3	1.0	2.84	0.58	0.71	95
	375	33.3	1.0	5.23	0.96	0.60	97
	425	33.3	1.0	6.25	1.35	0.49	98
	$E_{app.}$=8.5 kcal/mole				E=4.0 kcal/mole		
2,8-Dimethyl-5-thianonane $(CH_3-CH-CH_2-CH_2-)_2S$	325	33.3	1.0	2.2	0.47	0.79	92
	375	33.3	1.0	4.3	0.78	0.65	94
	425	33.3	1.0	8.0	1.24	0.60	98
	$E_{app.}$=11.0 kcal/mole				E=5.8 kcal/mole		
Dibenzyl sulfide 	325	33.3	1.36	4.7	1.32	0.58	92
	375	33.3	1.50	9.4	2.2	0.42	93
	425	33.3	1.50	18.2	2.9	0.37	95
	$E_{app.}$=11.3 kcal/mole				E=2.7 kcal/mole		
Thianaphthene	375	33.3	1.0	3.8	0.78	0.70	93
2,4,6,8-Tetramethyl-5-thianonane $(CH_3-CH-CH_2-CH-)_2S$	375	33.3	1.0	5.81	1.06	0.57	97
1,3-Dimethyl-1-(phenylthio)-butane 	375	33.3	1.0	5.88	1.11	0.56	96
α-(1-Phenyl)-propylthiophane 	375	33.3	1.0	8.14	1.61	0.52	96

* The general form of Frost's equation is $v_0 \ln \frac{1}{1-y} = \alpha + \beta v_0 y$, where v_0 is the mean rate of input of the starting compound into the reactor per gram of catalyst per hour, y is the extent of hydrogenolysis as a fraction, and α and β are parameters.

The general form of Kazaeev's equation is $\ln (D/D-M) = a\tau^b$, where τ is the conventional contact time in sec, M is the extent of hydrogenolysis in percent, D is the limiting value of M at $\tau \to \infty$, and a and b are parameters.

TABLE 2

Temp., °C	Parameter h		Diffusion retardation factor, f		Reaction rate constant, mole/g·hr		Apparent activation energy, kcal/mole	
	mean grain size of catalyst				observed	corrected	observed	corrected
	0.3 cm	0.06 cm	0.3 cm	0.06 cm				
325	1.65	0.33	0.56	0.965	0.62	1.10		
375	2.35	0.47	0.42	0.93	1.34	3.19	10.8	16.6
425	3.60	0.72	0.28	0.86	2.29	8.18		

dibenzothiphene, but were hardly affected by the addition of hydrogen sulfide (Fig. 3). Dibenzothiophene and its derivatives form a considerable part of the so-called "residual sulfur." Therefore, the data obtained are of interest in petroleum processing practice, as hydrofined fuels contain aromatic hydrocarbons in varying amounts.

By special experiments we established that in the presence of aluminum–cobalt–molybdenum catalyst at the temperatures and pressures used in industry, the hydrogenolysis proceeds in the diffusion region and it was shown that when the catalyst was made finer, the reaction moved into the transition region (Table 2). To a certain extent these data provide a theoretical basis for the fact that it is profitable to carry out hydrofining in a fluid bed. In addition, the data obtained may find practical application in the development of new recipes for preparing hydrofining catalysts.

A detailed analysis of the catalyzates showed that the main hydrogenolysis products from all the organosulfur compounds we studied were hydrogen sulfide and the corresponding hydrocarbon. Monocyclic aromatic hydrocarbons such as biphenyl [4] are not hydrogenated appreciably under the conditions we studied.

These observations provide a basis for the possibility of using an aluminum–cobalt–molybdenum catalyst for the analysis and identification of organosulfur compounds in petroleum products from their hydrogenolysis products, as is done with Raney nickel.

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SYNTHESIS OF ETHYLMERCURY SALTS

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Ethylmercury salts, C_2H_5HgX (where X is Cl, PO_4, etc.), are valuable fungicides. The industrial method of preparing ethylmercury salts is based on the reaction between HgX_2 and diethylmercury, which in its turn is obtained from low-percent sodium amalgam and ethyl bromide [1-4]. In addition, the compounds C_2H_5HgX may be synthesized through organomagnesium compounds [1] and also by the action of tetraethyllead on mercury phosphate [5], etc. [2].

Our method of preparing ethylmercury salts is based on the decarboxylation of mercuric propionate under the action of peroxides or ultraviolet light.

$$C_2H_5COOHgOCOC_2H_5 \xrightarrow[\text{or light}]{\text{peroxide}} C_2H_5HgOCOC_2H_5 + CO_2.$$

The anion in ethylmercuric propionate is readily replaced by any other anion.

The highest yields of ethylmercuric propionate (86.8%) were obtained by reaction of mercuric propionate with propionyl peroxide in propionic acid at 97-98°. The reaction was carried out in the following way. To a heated solution of 10.4 g (0.03 mole) of mercuric propionate in 100 ml of propionic acid was added a solution of 8.75 g (0.06 mole) of propionyl peroxide in 40 ml of propionic acid * over a period of 2 hours. When all the peroxide had been added, heating and stirring were continued for a further 1.5 hours. At the end of the reaction, the propionic acid was distilled from the reaction mixture under reduced pressure and the residue dissolved in water and treated with potassium chloride solution to yield ethylmercuric chloride. The weight was 4.89 g (61.5% yield) and the m.p. 194°. Treatment of the mother liquor with potassium iodide solution yielded a further 2.92 g of ethylmercuric iodide (27.3% yield) with m.p. 181°. The total yield of ethylmercury salts was 88.8%.

The propionyl peroxide required for the reaction could be prepared directly in the reaction mixture. To a mixture of 10.4 g of mercuric propionate (0.03 mole), 100 ml of propionic acid, and 40 ml of propionic anhydride was added 10 ml of 42% hydrogen peroxide over a period of 20 min at room temperature with stirring. The mixture was stirred at room temperature for a further 25 minutes and then heated on a boiling water bath. Heating and stirring were continued for 2 hours, and then 5.57 g of ethylmercuric chloride (70.0%) and 0.68 g of ethylmercuric iodide (6.35%) were isolated from the reaction mixture by the method described above. In this case, the total yield of ethylmercuric salts was 76.3% of the theoretical.

* The propionic acid solution of propionyl peroxide was prepared by the addition of 10 ml of 27% hydrogen peroxide to a mixture of 52 g of propionic anhydride and 2 g of solid sodium hydroxide over a period of 1 hour with cooling with snow and water and vigorous stirring.

Mercuric propionate is also decarboxylated under the action of ultraviolet light. A solution of 10.4 g of mercuric propionate in 150 ml of boiling propionic acid was irradiated for 80 minutes with a PRK-4 mercury–quartz lamp in the apparatus described previously [6]. The ethylmercury salts were isolated by the method described above. We obtained 7.27 g of ethylmercuric iodide (68.0% yield).

It should be noted that the yields of ethylmercury compounds obtained in the photochemical reaction depended strongly on the irradiation time, as the salt did not react completely with insufficient irradiation, while with longer irradiation, the ethylmercuric propionate formed underwent further decomposition to form metallic mercury. The method of preparing ethylmercury salts from mercuric propionate and propionyl peroxide is free from this drawback. Mercuric propionate may also be decomposed by other peroxides, for example, benzoyl peroxide. However, this leads to a fall in the yield of ethylmercury compounds and their contamination with phenylmercury salts.

Thus, mercuric propionate is best decarboxylated by propionyl peroxide, which may be prepared directly in the reaction mixture. This method makes it possible to obtain ethylmercury salts in high yields.

Work on the preparation of alkylmercury compounds is continuing.

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HIGH-TEMPERATURE CONDENSATION OF TETRACHLOROETHYLENE WITH AROMATIC HYDROCARBONS AND OLEFINS

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Schmerling and West [1, 2] showed that di- and trichlorovinyl groups may be introduced into the molecules of paraffins, isoparaffins, and alkylbenzenes by the condensation of tri- or tetrachloroethylene with the hydrocarbons listed under a nitrogen pressure of 50 atm with the reaction initiated with tert-butyl peroxide. The main products from the reactions of tri- and tetrachloroethylene with propane are 1,1-dichloro-3-methyl-1-butene and 1,1,2-trichloro-3-methyl-1-butene respectively, and 75-80% of them are present in the reaction products. In addition to the chloroolefins, 1,1-dichloro-1-pentene and 1,1,2-trichloro-1-pentene are evidently formed. The reaction with isobutane proceeds analogously and in this case, replacement of hydrogen by chlorovinyl groups occurs mainly at the tertiary carbon atom. The reaction of toluene with tri- and tetrachloroethylene forms only 2,3,3-trichloroallylbenzene and 3,3-dichloroallylbenzene and the reaction of trichloroethylene with ethylbenzene forms 3,3-dichloro-1-methylallylbenzene, i.e., replacement of the hydrogen by di- or trichlorovinyl groups occurs at the α-carbon atom of the side chain [2]. However, these authors were unable to introduce a trichlorovinyl group into an aromatic nucleus. The reaction of tetrachlorethylene with benzene under the conditions described above yielded only a small amount of hexachlorobutadiene. The yields of chlorovinylation products were 1.3-2.5 moles per mole of peroxide (18-45%) [2].

In the present work we describe a new method of synthesizing chlorohydrocarbons, containing a trichlorovinyl group. This method consists of the reaction of hydrocarbons with tetrachloroethylene in an empty quartz tube (flow system) at 550-590°. The reaction probably proceeds according to the following scheme:

$$Cl_2C=CCl_2 \rightarrow Cl_2C=\dot{C}Cl + Cl\cdot,$$
$$Cl\cdot + RH \rightarrow HCl + R\cdot,$$
$$Cl_2C=\dot{C}Cl + R\cdot \rightarrow R-CCl=CCl_2.$$

It was previously established that trichloroallyl alcohol is formed by the reaction of tetrachloroethylene with methyl alcohol at 570° [3]. It was found that this reaction is more general. By passing a mixture of benzene and tetrachloroethylene through a tube, we were able to obtain trichlorovinylbenzene in 14.4% yield, calculated on the starting materials, and 55% yield, calculated on the benzene consumed. Part of the benzene was converted into biphenyl: $C_6H_6 + Cl_2C=CCl_2 \rightarrow C_6H_5CCl=CCl_2 + C_6H_5-C_6H_5 + HCl$. The reaction of benzene with trichloroethylene proceeded similarly and dichlorovinylbenzene was formed as a result. When tetrachlorethylene reacted with alkylbenzenes (toluene, ethylbenzene, isopropylbenzene, and p-xylene), the trichlorovinyl group only entered the alkyl radical and there was no replacement of a hydrogen atom in the benzene nucleus under these conditions.

$$C_6H_5-\underset{\underset{H\,(CH_3)}{|}}{CH} + Cl_2C=CCl_2 \xrightarrow{530-570°} C_6H_5-\underset{\underset{H\,(CH_3)}{|}}{C}-CCl=CCl_2 + HCl.$$

TABLE 1

Expt. No.	Hydrocarbon	Amounts of components taken for reaction, hydrocarbon : tetrachloroethylene in moles	Temp. °C	Input rate		Time in reaction zone, sec	Yield, %
				g/hr	liter/liter·min		
1	C_6H_6	1.9 : 1.9	590	28.5	1.41	42.5	14.4
2	$C_6H_5CH_3$	0.56 : 0.56	570	45.5	3.08	19.5	5.7
3	$C_6H_5CH_3$	0.48 : 0.48	570	25.2	1.94	30.8	7.7
4	$C_6H_5CH_3$	0.49 : 0.49	570	17.9	1.19	50.2	18
5	$C_6H_5CH_3$	1 : 1	590	33.6	1.48	40.7	10
6	$C_6H_5CH_3$	0.5 : 1	550	39.7	1.6	37.5	19.4
7	p-$CH_3C_6H_4CH_3$	0.75 : 0.75	570	28.2	1.67	36	12.5
8	$C_6H_5CH_2CH_3$	0.5 : 0.5	550	28.6	1.77	34	21.2
9	$C_6H_5CH_2CH_3$	1 : 2	550	24.0	1.38	43.5	28.7
10	$C_6H_5CH(CH_3)_2$	1.5 : 1.5	560	30.8	0.52	115	11.8
11	$C_6H_5CH(CH_3)_2$	1 : 1	570	26	1.56	38.5	14.6
12	$CH_2{-}CH{=}CH_2$	1 : 1	550	26.7	0.63	96.6	11.1
13	$CH_2{-}CH{=}CH_2$	2.5 : 0.5	590	32.6	1.28	47	24.5
14	$(CH_3)_2C{=}CH_2$	1.3 : 1	580	30.9	0.72	83.3	16.2
15	$(CH_3)_2C{=}CH_2$	1.4 : 0.7	580	22	0.58	103.4	22.8
16	C_3H_6 •	2 : 1	570	26	1.56	38.4	11.5
17	$C_6H_5CH_3$ •	0.5 : 0.5	550	26.3	0.95	63.1	11.9

•Second component trichloroethylene.

The infrared spectrum of the product from the reaction of tetrachloroethylene with toluene was plotted. The position of the overtones of nonplanar C–H oscillation in the region of 5-6 μ corresponded to those normally observed for monosubstituted benzenes [4].

In the reaction of tetrachloroethylene with ethylbenzene and isopropylbenzene, the trichlorovinyl radical evidently replaced hydrogen not only at the α-, but also at the β-carbon atom of the side chain. Table 1 gives the experimental conditions and the yields of products from the condensation of tetrachloroethylene and trichloroethylene with benzene, alkylbenzenes, propylene, and isobutylene. The yields were calculated on the amounts of components taken for the reaction. When calculated on the materials consumed, the yield of trichlorovinylbenzene was 50%, of dichlorovinylbenzene 20-50%, of trichloroallylbenzene 50-80%, of the condensation product of tetrachloroethylene with ethylbenzene 40-75%, and of the condensation product with isopropylbenzene 20-45%. In the reaction of tetrachloroethylene with toluene at 570° with an equimolecular ratio of the components, we obtained the best results in experiment No. 4, where the rate at which the substances were passed through the tube was 1.19 min^{-1}. An increase in the rate led to a fall in the reaction product yield. The yield of trichlorosallylbenzene increased appreciably if the amount of tetrachloroethylene in the starting mixture of reaction components was twice that of toluene (experiment No. 6). A similar picture was observed in experiments on the condensation of tetrachloroethylene with ethylbenzene. In the interaction of tetrachloroethylene with propylene and isobutylene the reaction occurred at the methyl group, and dienes with the multiple bonds in the 1,4-position were formed as a result.

$$Cl_2C{=}CCl_2 + CH_3{-}CH{=}CH_2 \rightarrow Cl_2C{=}CCl{-}CH_2{-}CH{=}CH_2 + HCl.$$

The terminal position of the double bond in the hydrocarbon part of the molecule of 1,1,2-trichloro-1,4-pentadiene was confirmed by the Raman spectrum, in which the frequencies of 1640 and 3085 cm^{-1} were detected. The yields of $Cl_2C{=}CCl{-}CH_2{-}CH{=}CH_2$, calculated on the tetrachloroethylene consumed in the reaction, were 45-60% and those of $Cl_2C{=}CCl{-}CH_2{-}C(CH_3){=}CH_2$, 55-65%. An attempt to prepare $Cl_2C{=}CCl{-}CH{=}CH_2$ under analogous conditions by the reaction of $Cl_2C{=}CCl_2$ with ethylene was unsuccessful. Coke and soot formation in the reaction tube was observed in all experiments. After the starting materials and condensation product has been isolated from the reaction mixture, a solid or resinous material remained. With equimolecular ratios of the reagents, when the amount of each was 1 mole, the greatest residues were observed in the reactions of tetrachloroethylene with isopropylbenzene (20-30 g), ethylbenzene (6-15 g), toluene (3-6 g), propylene (4-5 g), and isobutylene (4-5 g). The properties of the condensation products are given in Table 2.

TABLE 2

Condensation product	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc	Found % C	Found % H	Calc. % C	Calc. % H
$C_6H_5CH=CCl_2$	89–90/9	1.2531	1.5852	46.29	44.94	55.29 55.20	3.54 3.54	55.53	3.49
$C_6H_5CCl=CCl_2$	97–98/7	1.3728	1.5932	50.53	49.77				
$C_6H_5CH_2CH=CCl_2$	87–88.5/5	1.2035	1.5540	49.51	49.39				
$C_6H_5CH_2-CCl=CCl_2$	80–82/2	1.3150	1.5936	54.55	54.42				
$p-CH_3-C_6H_4-CH_2CCl=CCl_2$ *	123–124/7	1.2760	1.5571	59.43	59.06	51.18 50.84	3.95 4.07	51.00	3.85
$C_6H_5CH(CH_3)CCl=CCl_2$ *	80–82/2	1.2883	1.5611	59.29	59.07	51.50 51.50	3.88 3.80	51.00	3.85
$C_6H_5-C(CH_3)_2CCl=CCl_2$ *	84–88/2	1.2756	1.5645	63.48	63.73				
$CH_2=CH-CH_2-CCl=CCl_2$ *	54–55/20	1.2894	1.4952	38.79	38.84	35.32 35.30	3.19 2.96	35.01	2.94
$CH_2=C(CH_3)-CH_2-CCl=CCl_2$ *	167–168	1.2380	1.4967	43.73	43.49	39.08 39.24	3.92 3.99	38.85	3.80

* Obtained for the first time.

EXPERIMENTAL

All the high-temperature condensations were carried out in an empty quartz tube in a catalytic electric furnace. Two furnaces were used: one with a length of 600 mm and an internal diameter of 40 mm and one with a length of 995 mm and an internal diameter of 35 mm. In the short furnace we carried out experiments with tubes with diameters of 18.5 mm (experiments No. 3-5, 7-9, 11, 16, and 17) and 22.5 mm (experiments No. 1, 2, and 6) and in the long furnace with a tube 26 mm in diameter (experiments No. 10 and 12-15). The working part of the tube was 100 mm less than the length of the furnace. The temperature was measured within the reaction tube in the middle. The space velocity of the reagent vapors was calculated from the formula $V = nK/\tau v$, where n is the number of moles of the substances passed through the tube in time τ, v is the volume of the reaction tube (in liters), and K is the volume of the vapor of one mole of substance at the experimental temperature (assuming that the starting materials and substances formed obey the gas laws at 530-590°). A prepared mixture of the reaction components was passed into the tube, but in the reaction of tetrachloroethylene with propylene and isobutylene, the components were passed into the tube separately. At the outlet of the furnace, the vapors were condensed with an air condenser and then in a water condenser. The reaction mixture was separated into components by distillation on a column. If the starting materials had similar boiling points, their ratio in the fractions distilled was determined from a graph of the relation between the percent composition of the mixture and the specific gravity or the refractive index. A detailed description of a few experiments is given below.

Trichlorovinylbenzene (experiment No. 1). Over a period of 16 hr 20 min, a mixture of 149 g (1.9 mole) of benzene and 315 g (1.9 mole) of tetrachloroethylene was passed through a tube 22.5 mm in diameter, at 590°. As a result we obtained 416 g of reaction mixture, from which we isolated 110 g (1.41 mole) of benzene, 200 g (1.2 mole) of tetrachloroethylene, and 57 g of a wide fraction, which consisted mainly of trichlorovinylbenzene with a trace of biphenyl. The residue (38 g) consisted of biphenyl with m.p. 70° (from alcohol). By fractional distillation and chromatography on a column packed with silica gel (100-200 mesh) we isolated pure trichlorovinylbenzene from the wide fraction, the yield of which was 14.4%, calculated on the starting materials.

2,3,3-Trichloroallylbenzene (experiment No. 4). Over a period of 7 hr 4 min a mixture of 45 g (0.49 mole) of toluene and 81 g (0.49 mole) of tetrachloroethylene was passed through a tube with an internal diameter of 18.5 mm, at 570°. As a result we obtained 117 g of a dark-brown liquid. On distillation, the reaction mixture yielded 35.4 g (0.38 mole) of toluene, 55 g (0.33 mole) of tetrachloroethylene, and 19.5 g of 2,3,3-trichloroallylbenzene (see Table 2 for properties). The yield calculated on the starting materials was 18%, on the toluene consumed, 50%, and on the tetrachloroethylene consumed, 55%. The high-boiling residue weighed 3 g.

1, 1, 2-Trichloro-1,4-pentadiene (experiment No. 13). Over a period of 5 hr 48 min, 83 g (0.5 mole) of tetrachloroethylene and 58 liters (2.5 mole) of propylene were passed through a tube 26 mm in diameter at 590°. From 72 g of the reaction mixture obtained, we isolated 44 g (0.265 mole) of tetrachloroethylene and 21 g of 1,1,2-trichloro-1,4-pentadiene. The yield calculated on the tetrachloroethylene taken for the reaction was 24.5 % and that calculated on the tetrachloroethylene consumed was 52%. The resinous residue weighed 3 g.

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REDUCTIVE DESULFURIZATION OF SOME DIAMINES OF THE THIOPHENE SERIES

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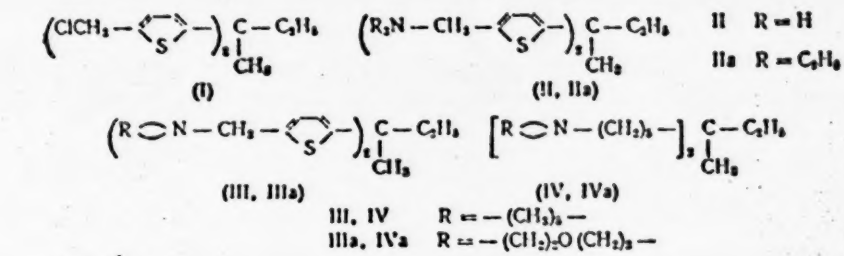
M. B. Ibragimova and one of us previously showed that by the action of Raney nickel on tertiary amines and amino alcohols of the thiophene series it was possible to obtain aliphatic amines [1] and amino alcohols [2] with a comparatively long chain of carbon atoms. It seemed interesting to extend the reductive desulfurization method to ditertiary amines of the thiophene series so as to obtain higher alkylenediamines, which could be used for the synthesis of the corresponding bis-ammonium salts with a potential curariform activity. In a certain sense, in comparison with decamethonium and related salts [3], haloalkylates of diamines IV and IVa, which have branching in the center of the chain, are a new type of these compounds. As far as we know, no bis-ammonium salts of this type have been described and there seem to be no suitable routes for synthesizing them from aliphatic compounds. Moreover, the presence of branching has a definite effect on the activity of some compounds with a curariform action [4].

As the starting compound for preparing the bases mentioned we used 2,2-bis-(2-thienyl)-butane, which is readily formed by the reaction of thiophene with methyl ethyl ketone [5]. Chloromethylation of it yielded the bischloromethyl derivative I, which was usually used in the "crude" state as it decomposed considerably during vacuum distillation. However, judging by the fact that the reaction with amines gave a product yield of the order of 60%, it can be assumed that chloromethylation proceeded quite satisfactorily. The action of hexamethylenetetramine on compound I yielded the corresponding salt, which was converted into diamine II by the usual method. Under quite mild conditions compound I reacted with diethylamine, piperidine, and morpholine to form diamines IIa, III, and IIIa, which gave diiodomethylates with methyl iodide.

As the hydrogenolysis of dialkylaminothiophenes could be carried out with Raney nickel [1], it seemed probable that this method could be used for preparing the higher diamines required. However, under these conditions we obtained mixtures which distilled over a wide range. This may have been connected with the capacity of Raney nickel to rupture the C—N bond. We, therefore, decided to use skeletal cobalt, which may be more suitable than skeletal nickel for the preparation of amines, though it is less active than the nickel [6, 7]. In actual fact, amines III and IIIa slowly lost sulfur when heated in methanol with a large excess of Co; when the desulfurization process was complete, it was possible to isolate diamines IV and IVa by the usual method. The yield of the latter in the experiments described below did not exceed 30%, though we have grounds for considering that it may be increased by some modification of the experimental conditions. The diiodomethylates of IV and IVa were prepared from the diamines mentioned. The investigation is being continued.

*Deceased.



(I) (II, IIa)

III, IV R = —(CH2)5—

IIIa, IVa R = —(CH2)2O(CH2)2—

EXPERIMENTAL

2,2-Bis-(5-chloromethyl-2-thienyl)-butane (I). A mixture of 33.3 g of freshly distilled 2, 2-bis-(2-thienyl)-butane, 50 ml of glacial acetic acid, and 35 g of chloromethyl ether was left at 20° for 16 hr and then heated with stirring for 2 hr on a water bath at 40°. After cooling, it was washed twice with ice water, dissolved in 150 ml of benzene, washed with sodium bicarbonate solution and water, and dried over calcium chloride. Removal of the solvent and distillation gave compound I in a yield of no higher than 27% and with b.p. 183-185°/1 mm.

Found %: C 52.73; 52.91; H 4.97; 5.20 $C_{14}H_{16}Cl_2S_2$. Calculated %: C 52.66 H 5.04

2,2-Bis-(5-aminomethyl-2-thienyl)-butane (II). The salt of I and hexamethylenetetramine, obtained from 12 g of distilled I and 10.3 g of urotropine in 100 ml of chloroform (standing for 2 days at 20°), was heated for 3 hr on a water bath with 30 g of concentrated hydrochloric acid in 200 ml of ethanol. Evaporation of the solvent gave the crystalline hydrochloride of II, which was made alkaline with 40% NaOH solution. The mixture was extracted with ether and benzene and the extracts dried with potassium carbonate. Removal of the solvent from the extracts yielded about 8 g of compound II with b.p. 200-215°/1 mm and 210-225°/3-4 mm. Redistillation gave 5.1 g (49%) of compound II with b.p.210-215°/1 mm.

Found %: C 60.30; 60.43; H 7.38; 7.32; N 9.93 $C_{14}H_{20}N_2S_2$. Calculated %: C 59.95; H 7.19; N 9.99

2,2-Bis-(5-diethylaminomethyl-2-thienyl)-butane (IIa). To a benzene solution of compound I, prepared from 33.3 g of 2,2-bis-(2-thienyl)-butane, was added 51 g of diethylamine and the mixture was kept at 20° for 16 hr and then heated at 60° for 2 hr. The precipitated crystals of diethylamine hydrochloride were removed by filtration and washed with benzene. The benzene solution of the amine was dried over BaO. After evaporation of the benzene and excess diethylamine, the residue was vacuum distilled (2 mm) to yield fraction 1 (up to 198°) (a few drops) and fraction 2 at 198-201° (37 g). Redistillation of fraction 2 gave 34.8 g of product with b.p. 194-195°/2 mm, i.e., 60% yield calculated on the starting 2,2-bis-(2-thienyl)-butane; it had $n^{20}D$ 1.5400; d^{20}_4 1.0241; MR_D found 120.28, calculated 119.93.

Found %: C 67.21; 67.34; H 9.43; 9.39; S 16.24; 16.24 $C_{22}H_{36}N_2S_2$. Calculated %: C 67.29; H 9.24; S 16.33

The dihydrochloride of IIa, purified by precipitation with absolute ether from a methanol—acetone solution, melted at 155-156° (in a sealed capillary).

Found %: N 6.06; 6.07 $C_{22}H_{38}N_2S_2Cl_2$. Calculated %: N 6.02

2,2-Bis-(5-piperidinomethyl-2-thienyl)-butane (III). To a benzene solution of I, prepared from 22.2 g of 2,2-bis-(2-thienyl)-butane and 27 g of chloromethyl ether, was added 34.0 of piperidine and the mixture left for 16 hr. The contents of the flask were then boiled under reflux for 2 hr. Further treatment was as in the previous experiment. Vacuum distillation (2 mm) of the product yielded fraction 1 up to 235° (1.1 g) and fraction 2 at 235-237° (27.3 g). Redistillation of fraction 2 at 2 mm gave 26.1 g of a colorless, viscous product with b.p. 245 to 246° [63% yield, calculated on the starting 2,2-bis-(2-thienyl)-butane], $n^{20}D$ 1.5653; d^{20}_4 1.0864; MR_D found 124.98; calculated 124.76.

Found %: C 69.19; 69.42; H 8.84; 8.92; S 15.43; 15.32 $C_{24}H_{38}N_2S_2$. Calculated %: C 69.18; H 8.71; S 15.39

The diiodomethylate* of III, purified by two reprecipitations with absolute ether from methanol solution, melted at 192.5-193.5°.

* All the iodomethylates were prepared by the action of excess methyl iodide on an ether solution of the base, with the exception of the iodomethylate of IIIa, which was prepared by boiling excess methyl iodide and the diamine in acetone.

Found %: C 44.45; 44.43; H 5.94; 5.93; I 35.22; 35.53 $C_{24}H_{42}I_2N_2S_2$. Calculated %: C 44.57; H 6.07 I 36.23

The picrate* of III melted at 185-186° after recrystallization from a mixture of acetone and heptane (1:1).

Found %: C 49.66; 49.60; H 5.00; 4.95; S 7.10; 7.28 $C_{36}H_{42}N_8O_{14}S_2$. Calculated %: C 49.41; H 4.83; S 7.31

2,2-Bis-(5-morpholinomethyl-2-thienyl)-butane (IIIa) was obtained from 35 g of morpholine and a benzene solution of I, prepared from 22.2 g of 2,2-bis(2-thienyl)-butane. After removal of the solvent the diamine was fractionated in vacuum (2 mm) to give fraction 1 up to 245° (0.93 g) and fraction 2 at 245-246° (28.9 g). Redistillation of fraction 2 yielded 26.2 g (62%) of a viscous liquid with b.p. 243-244°/2 mm. The product crystallized on storage and had m.p. 60-63°. The melting point was 65-66° after the substance had been recrystallized from heptane.

Found %: C 62.68; 62.76; H 7.74; 7.91; S 15.20; 15.38 $C_{22}H_{32}N_2O_2S_2$. Calculated %: C 62.82; H 7.67; S 15.24

The diiodomethylate of IIIa melted at 195-197° (with decomp. in a sealed capillary) after two recrystallizations from methanol.

Found %: C 40.79; 40.64; H 5.59; 5.43; I 35.39; 35.41 $C_{24}H_{38}I_2N_2O_2S_2$. Calculated %: C 40.91; H 5.44; I 36.02

The picrate of IIIa melted at 198-199° after two recrystallizations from a mixture of alcohol and acetone.

Found %: N 13.05; 13.22; $C_{34}H_{38}N_8O_{16}S_2$. Calculated %: N 12.82

N-Oxide of 2,2-bis-(5-morpholinomethyl-2-thienyl)-butane. A mixture of 1.34 g of IIIa and 20 ml of a 25% solution of H_2O_2 was stirred at 20° for 28 hr and then the water and excess hydrogen peroxide were removed by distillation on a water bath ** at 14 mm. The residue in the flask was dissolved in 50 ml of absolute alcohol, 0.5 g of manganese dioxide added, and the mixture boiled under reflux for 0.5 hr. The MnO_2 was removed by filtration, 100 ml of benzene added to the filtrate, and the solvents removed by distillation. There remained in the bottom of the flask a solid product which deliquesced in air. After it was recrystallized three times from a mixture of absolute alcohol and benzene, it had m.p. 152-153°.

Found %: N 6.00; 6.00 $C_{22}H_{32}N_2I_4S_2$. Calculated %: N 6.19

1,11-Dipiperidino-6-methyl-6-ethylundecane (IV). A mixture of 12 g of compound III, 700 ml of methanol, and 180 g of skeletal cobalt *** was stirred at 20° for 5 hr and then boiled under reflux for 40 hr (until a sulfur test was negative). The cobalt was removed by filtration and washed with hot ethanol. After evaporation of the alcohol, the residue was extracted with ether and dried over BaO. The ether was removed and the residue distilled (4 mm) to yield fraction 1 at 152-201° (2.6 g) and fraction 2 at 201-204° (3.8 g). Redistillation of fraction 2 gave 3.6 g of a colorless, viscous liquid with b.p. 199-202°/4 mm (34% yield). $n^{20}D$ 1.4836; d^{20}_4 0.8991; MR_D found 115.94, calculated 116.51.

Found %: N 7.67; 7.77 $C_{24}H_{48}N_2$. Calculated %: N 7.61

The molecular weight found was 369 and the calculated value, 364.6.

The diiodomethylate of IV had m.p. 179.5-180.5° (from acetone).

Found %: C 47.91; 47.74; H 8.14; 8.29; I 38.49; 38.43 $C_{26}H_{54}I_2N_2$. Calculated %: C 48.15; H 8.39; I 39.14

The picrate of IV had m.p. 121.5-122.5° (from alcohol).

Found %: N 13.90; 13.93 $C_{38}H_{54}N_8O_{14}$. Calculated %: N 13.67

1,11-Dimorpholino-6-methyl-6-ethylundecane (IVa) was obtained similarly to compound IV from 12 g of compound IIIa in 600 ml of methanol by the action of 255 g of skeletal cobalt. The hydrogenolysis product was

* The picrates were prepared by mixing hot alcohol solutions of picric acid and the corresponding diamine.

** The bath temperature should not exceed 50°.

*** The skeletal cobalt was prepared from 50% cobalt–aluminum alloy by the procedure proposed by Adkins and Billick [8] for the preparation of Raney nickel.

vacuum distilled (5 mm) to give fraction 1 up to 223°(2.3 g) and fraction 2 at 223-226° (3.6 g). Redistillation of fraction 2 gave 3.3 g of product with b.p. 202-206°/4 mm (31% yield); $n^{20}D$ 1.4830; d^{20}_4 0.9487; MR_D found 110.56, calculated 110.97.

Found %: C 71.31; 71.60; H 11.99; 11.92 $C_{22}H_{44}N_2O_2$. Calculated %: C 71.74; H 12.03

The difiodomethylate of IVa had m.p. 193.5-196.5° (with decomp., in a sealed capillary) after two recrystallizations from acetone.

Found %: C 44.18; 43.85; H 7.67; 7.61; I 38.44; 38.34 $C_{24}H_{50}I_2N_2O_2$. Calculated %: C 44.16; H 7.73; I 38.90

The picrate of IVa had m.p. 135.5-136.5° (from methanol)

Found %: N 12.92; 13.14 $C_{34}H_{52}N_8O_{14}$. Calculated %: N 13.55

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RADIATION METHOD OF SYNTHESIZING SOME DERIVATIVES OF PHOSPHONITRILE CHLORIDE

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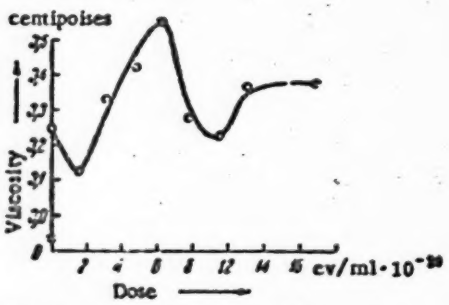
Among the inorganic polymeric compounds which have plastic properties, phosphonitrile chloride, $(PNCl_2)_n$, is of the greatest interest [1-8]. However, the practical use of this comparatively heat-stable polymer is hampered by the fact that it hydrolyzes quite readily. The introduction of certain organic substituents, e.g., alkoxyl radicals) into the phosphonitrile chloride molecule leads to a considerable increase in its hydrolysis resistance [9, 10]. However, prolonged heating of the reagent mixture is normally required for the preparation of such derivatives. The yields in this case are generally low. For example, [9], n-butyl phosphonitrile ether $[PN(OC_4H_9)_2]_x$ is formed only after a mixture of phosphonitrile chloride, n-butyl alcohol, and sodium or potassium butylate is heated at 117° for 13 hours.*

At the present time the action of penetrating radiation is finding increasing application in the synthesis of organic compounds [11] and the preparation of inorganic products [12]. We investigated the possibility of synthesizing butyl phosphonitrile ether by irradiating a mixture of phosponitrile chloride tetramer and n-butyl alcohol at room temperature with a beam of high-energy electrons.



Change in viscosity of a 5% solution of phosphonitrile chloride tetramer in n-butyl alcohol in relation to the integral radiation dose.

Phosphonitrile chloride tri- and tetramer were synthesized by the procedure in [13]. The butyl alcohol was first purified and dried. The radiation source was a 1.0-1.2 Mev electron accelerator, consisting of a vertical, sectional tube of a direct accelerator and a voltage multiplier rectifier-condenser cascade [14]. The solutions were irradiated in glass cells with a thin glass membrane. The dose strength was checked by measuring the electron current in the solution with the aid of a molybdenum probe sealed into the cell. In experiments with n-butyl alcohol, air saturated with n-butanol was passed through the cell to cool the solution and give steady stirring. The course of the reaction was followed by the change in viscosity of the solution, measured with an Ostwald viscometer, and also by determining the chlorine content of the compounds formed. It was established that under the action of a beam of fast electrons on solutions of

* The author of [9] did not give the yield of the reaction product. We repeated the procedure described by him and found that the yield was only 23%.

TABLE 1

Change in Viscosity and Chlorine Content of a 5% Solution of Phosphonitrile Chloride Tetramer in n-Butanol in Relation to the Integral Dose of Electron (0.6 Mev) Radiation.

Irradiation time, min	Integral radiation dose, ev/ml	Solution viscosity, centipoise	Chlorine content,* %	Irradiation time, min	Integral radiation dose, ev/ml	Solution viscosity centipoise	Chlorine content,* %
0	0	3,243	100	10	$8,0 \cdot 10^{20}$	3,274	22,8
2	$1,6 \cdot 10^{20}$	3,126	24,7	12	$9,6 \cdot 10^{20}$	3,252	16,2
4	$3,2 \cdot 10^{20}$	3,329	23,2	14	$1,1 \cdot 10^{21}$	3,357	14,5
6	$4,8 \cdot 10^{20}$	3,417	27,8	20	$1,6 \cdot 10^{21}$	3,362	13,8
8	$6,4 \cdot 10^{20}$	3,550	29,2				

* The chlorine content of the unirradiated solution was taken as 100%.

phosphonitrile chloride tetramer in n-butyl alcohol, both chlorine atoms in the phosphonitrile chloride molecule were replaced by butoxyl radicals.

A description of a typical experiment on the isolation of butyl phosphonitrile ether is given below. A sample (80 ml) of a 5% solution of phosphonitrile chloride tetramer in absolute n-butyl alcohol was irradiated for 6 hr with 0.6 Mev electrons at a beam strength of 3 μa in the solution. The integral dose was $1.5 \cdot 10^{22}$ ev/ml. Air was passed through the solution during irradiation. The temperature did not exceed 30° during the experiment. after irradiation, the n-butanol was distilled in vacuum with heating on a water bath. The residue was a viscous brown liquid with an unpleasant smell. Its analysis corresponded to that of n-butyl phosphonitrile ether:

Found %: C 50.10; H 9.04 $[PN(OC_4H_9)_2]_x$. Calculated %: C 50.25; H 9.42

The product yield was 45%, i.e., almost twice as great as by the method in [9].

Table 1 gives the results of measuring the viscosity of irradiated 5% solution of tetramer in n-butyl alcohol and determining the chlorine content of the products obtained. The average values from 2-4 measurements are given. The error in the viscosity determination did not exceed 1%.

Figure 1 shows the characteristic change in the viscosity of a 5% butanol solution of tetramer in relation to the integral radiation dose. The radiolytic interaction of phosphonitrile chloride with n-butyl alcohol evidently is complex. The sharp fall in chlorine content and the decrease in viscosity in the initial moment of irradiation is evidently caused by a chain substitution reaction. The dissolved substance probably reacted mainly with hydrogen atoms produced by radiolysis of n-butyl alcohol (for example, according to the scheme $CH_3CH_2CH_2CH_2OH \rightarrow$ $\rightarrow CH_2CH_2CH_2CHOH + H$). As a result of reaction with atomic hydrogen, the tetramer ring is ruptured with the formation of monomer and dimer radicals and the elimination of a chlorine atom in the form of HCl.

$$4H + (PNCl_2)_4 \rightarrow 2(PNCl)_2 + 4HCl \quad (1)$$

or

$$4H + (PNCl_2)_4 \rightarrow 4PNCl + 4HCl, \quad (1a)$$

$$H + PNCl \rightarrow PN + HCl, \quad (2)$$

$$PNCl + C_4H_9OH \rightarrow PN(OC_4H_9)_2 + HCl, \quad (3)$$

$$PNOC_4H_9 + C_4H_9OH \rightarrow PN(OC_4H_9)_2 + H, \quad (4)$$

$$PN + 2C_4H_9OH \rightarrow PN(OC_4H_9)_2 + 2H. \quad (5)$$

The hydrogen atoms formed by reactions (4) and (5) again react with tetramer, etc.

However, with further irradiation, together with cyclization, there is also the possibility of the reverse reaction between HCl and butoxy derivatives due to the high concentration of hydrogen chloride formed. This is indicated by the chlorine analysis results (Table 1). A maximum therefore appears on the curve in Fig. 1. The

TABLE 2

Analysis of Compounds Obtained from Dioxane Solution of Phosphonitrile Chloride Trimer

Experiment Number	Trimer concentration in dioxane, %	Experimental conditions		Analysis results, %	
		integral radiation dose, ev/ml	reaction time	C	H
1	3	–	3 months	26.71	4.52
2	2	$1.6 \cdot 10^{22}$	2 hours	26.82	4.34
	Calculated for $(PNClC_4H_8O_2)_x$			28.48	4.75

second minimum is evidently caused by suppression of the reverse reaction. The increase in viscosity at high values of the integral radiation dose are probably explained by cyclization of the butoxy derivative with the subsequent formation of polymeric molecular chains.

The radiation method of synthesizing butyl phosphonitrile ether has a number of advantages in comparison with the normal methods of synthesizing it, namely the higher yield, the ease of isolation from the reaction mixture, and the low reaction temperature.

The effect of ionizing radiation on a 2% solution of phosphonitrile chloride trimer in absolute dioxane was also studied. During irradiation with 0.8 Mev electrons, the viscosity of the dioxane solution first increased considerably and then the formation of a white, flocculent precipitate was observed. A similar result was also obtained when the starting solution was kept for a long period (3 months). The residue was analyzed after the dioxane had been removed in vacuum (Table 2).

According to the analysis results, the substance formed in dioxane had the composition $(PNClC_4H_8O_2)_x$, i.e., was the product from the substitution of one chlorine atom of phosphonitrile chloride by a dioxane molecule. This compound had a considerable resistance to hydrolysis and was not decomposed even when boiled with alcoholic alkali. The structure of the compound obtained is being studied further.

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CATALYSIS OF HYDROGENATION REACTIONS BY ZINC

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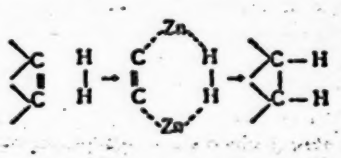
At the present time there is the widespread opinion that a heterogeneous catalytic reaction proceeds through an adsorption stage. If both components are activated in the hydrogenation process, they form a surface intermediate complex with the catalyst. In this case the ease of hydrogenation of the different interatomic bonds depends on the height of the energy barrier ($-E$) of the reaction [1]. In the first instance, there must exist a reaction for which the height of the energy barrier for the formation (or decomposition) of the intermediate complex is a minimum. The value of E may be calculated from the mean values of the bond energies (Q). Thus, for example, for the hydrogenation of C = C, C ≡ C, and C = O bonds on a Ni catalyst, they are respectively: $-E_{C=C} = 2{,}9$ kcal, $-E_{C\equiv C} = -7{,}4$ kcal, and $-E_{C=O} = 13{,}1$ kcal. In accordance with this, C ≡ C and C = C bonds are actually hydrogenated more readily on a Ni catalyst than C = O bonds. These reactions proceed in an analogous sequence on almost all known catalysts.

A completely different picture is observed on Zn, on which C = C bonds are not hydrogenated as a rule, while the C = O group is hydrogenated to CH–OH and an acetylene bond is selectively hydrogenated to an ethylene bond.

Let us see if these interesting characteristics of Zn cannot be explained also by the relative heights of the energy barriers of the reactions on this catalyst. The hydrogenation of an ethylene bond on Zn with the formation of an intermediate complex is illustrated by the scheme:



Its heat of formation:

$$E_1^{\circ} = -Q_{C=C} - Q_{H-H} + 2Q_{=C-Zn} + 2Q_{H-Zn} =$$
$$= -46{,}7 - 104{,}2 + 2 \cdot 27 + 2 \cdot 19{,}5 = -57{,}9 \text{ kcal/mole.} \quad (I)$$

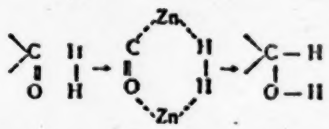
Its heat for decomposition $E_1^{\circ} = -2Q_{=C-Zn} - 2Q_{H-Zn} + 2Q_{C-H} = -2 \cdot 27 - 2 \cdot 19{,}5 + 2 \cdot 90{,}5 = 88$ kcal/mole.

Similarly, for the hydrogenation of an acetylene bond to an ethylene bond, the heat of formation:

$$E_2^{\circ} = -Q_{C\equiv C} - Q_{H-H} + 2Q_{=C-Zn} + 2Q_{H-Zn} =$$
$$= -37{,}4 - 104{,}2 + 2 \cdot 27 + 2 \cdot 19{,}5 = -48{,}6 \text{ kcal/mole} \quad (II)$$

The heat of decomposition: $E_2^{\cdot} = -2Q_{=C-Zn} - 2Q_{H-Zn} + 2Q_{C-H} = -54 - 39 + 181 = 88$ $\frac{\text{kcal}}{\text{mole}}$.

The double scheme for the reduction of a C = O group is as follows:



The heat of formation of the complex:

$$E_3^{\cdot} = -Q_{C=O} - Q_{H-H} + Q_{=C-Zn} + Q_{O-Zn} + 2Q_{H-Zn} =$$
$$= -83,4 - 104,2 + 27 + 74,2 + 2 \cdot 19,5 = -47,4 \text{ kcal/mole} \qquad \text{(III)}$$

Its heat of decomposition: $E_3^{\cdot} = -Q_{C-Zn} - Q_{O-Zn} - 2Q_{H-Zn} + Q_{C-H} + Q_{O-H} = -27 - 74.2 - 2 \cdot 19.5 + 90.5 + 110.4 = 60.7$ kcal/mole. Instead of $Q_{=C-Zn}$ and $Q_{\equiv C-Zn}$, for which there are no literature data, we used the somewhat lower bond energy Q_{-C-Zn}, which probably had no effect on the basic result.

As can be seen, for all three reactions $E^{\cdot} < 0$ and $E^{\cdot} > 0$. Consequently, the rate of these processes must be limited by the adsorption stage [1]. From the approximate calculations presented it follows that the energy barriers of the reaction of Zn considered are considerably higher than on Ni. If it is assumed that $E = {}^{4}/_{5}\epsilon$, then their activation energies are 43.39 and 26 kcal/mole, respectively. By changing the signs for E, we obtain $-E_{C=C} = 57.9$ kcal/mole, $-E_{C\equiv C} = 48.6$ kcal/mole, and $-E_{C=O} = 47.4$ kcal/mole. These results make it possible to predict that all three reactions on Zn should proceed with much more difficulty than on Ni and other metallic hydrogenation catalysts. As $|E'_1| > |E'_2| > |E'_3|$, then it should be most difficult to hydrogenate the ethylene bond and easier to hydrogenate the C=O bond. The bond energy Q_{H-Zn} was taken from [2] and the other bond energies from [3]. Q_{O-Zn} was calculated in our laboratory.

Analysis of equations (I)–(III) shows that the higher values of E' on Zn in comparison with E' on Ni are caused by the fact that Q_{H-Zn} (19.5 kcal) $< Q_{H-Ni}$ (55 kcal), though Q_{-C-Zn} (27 kcal) > $Q_{=C-Ni}$ (19 kcal) and Q_{O-Zn} (74.2 kcal) > Q_{O-Ni} (48.3 kcal). This indicates that the ratio of the concentrations of active hydrogen and compound hydrogenated on Zn is lower than on Ni.

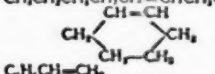
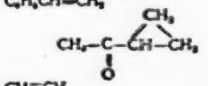
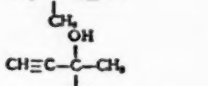
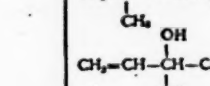
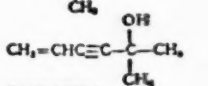
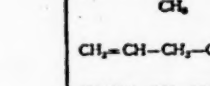
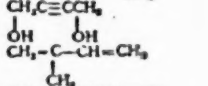
EXPERIMENTAL

The catalyst was prepared by leaching turnings of fine platelets of Zn–Al alloy (weight ratio of 1:1) with a 3% aqueous solution of sodium hydroxide until the evolution of hydrogen ceased, then washing with water to a neutral reaction to phenolphthalein, and it was loaded into the reactor in a moist state. The catalyst was found to contain 5% of residual Al. In all operations we tried to prevent contact of the catalyst with air. Experiments at normal pressure were carried out under flow conditions. The compound hydrogenated (and a large excess of hydrogen) was passed over the catalyst at a space velocity of 0.1–0.2. In experiments under pressure, the reaction was carried out in a rotating autoclave. The catalyst was normally used once. The degree of unsaturation of the catalyzates and their carbonyl group content (by the oxime method) were determined. The degree of unsaturation was characterized by the volume of hydrogen consumed in the hydrogenation of a sample of catalyzate on skeletal nickel at 20°. In other cases, the catalyzates were also analyzed by gas–liquid chromatography or fractionation on a column. The constants of the reaction products isolated were determined. The table gives the conditions under which hydrogenation of the three types of bond (C = C, C ≡ C, C = O) in the compounds we investigated began.

Hydrogenation of the Ethylene Bond. At temperatures up to 200°, 2- and 3-octenes were recovered unchanged. 1-Octene and cyclohexene were not hydrogenated under a pressure of 100 atm at 150°.

Styrene did not add hydrogen at temperatures below 100° and normal pressure. The rate of the reaction increased sharply above 170°.

At 250° the degree of hydrogenation of styrene reached 98%. The catalyzate was vacuum distilled and was found to be almost pure ethylbenzene with b. p. 135°/740 mm, $n^{20}D$ 1.4950; d^{20}_4 0.8660. The residue after

Compound hydrogenated	Main reaction product	Bond hydrogenated	Temp., °C*	Pressure, atm*
$CH_3CH_2CH_2CH_2CH_2CH_2CH=CH_2$	Not hydrogenated	α-C=C	150	100
$CH_3CH_2CH_2CH_2CH_2CH=CHCH_3$	Not hydrogenated	β-C=C	200	Normal
$CH_3CH_2CH_2CH_2CH=CHCH_2CH_3$	Not hydrogenated	γ-C=C	200	Normal
	Not hydrogenated	Ring C=C	150	100
$C_6H_5CH=CH_2$	$C_6H_5C_2H_5$	Active C=C	100	Normal
	$CH_3CHOHCH-CH_2$	C=O	90	130
$CH\equiv CH$	$CH_2=CH_2$	C≡C	65	Normal
$C_6H_5C\equiv CC_6H_5$	$C_6H_5CH=CHC_6H_5$	C≡C	60	Normal
$CH_2=CHC\equiv CH$	$CH_2=CH-CH=CH_2$	C≡C	60	Normal
$CH_2=C-C\equiv CH$	$CH_2=C-CH=CH_2$	C≡C	50	Normal
		C≡C	50	Normal
		C≡C	80	100
$CH_3C\equiv CCH_3$	$CH_3OH-CH=CH-CH_2OH$	C≡C	130	90
	Not hydrogenated	Active C=C	140	Normal
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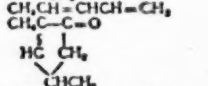
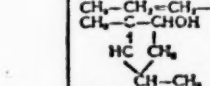
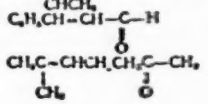
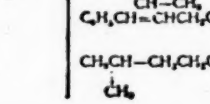
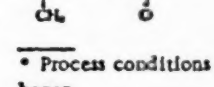
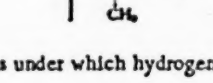
		C=O	50	Normal
		C=O	60	Normal
		C=C	100	Normal

* Process conditions under which hydrogenation of the given compound on the zinc catalyst began.

distillation was insignificant. Styrene was completely polymerized in an experiment at 100 atm and 100° after 3 hr. Zinc did not catalyze the hydrogenolysis of the trimethylene ring of methyl cyclopropyl ketone [4], which reacts readily with hydrogen on other metals and imitates the behavior of a double bond [5].

Hydrogenation of Diene Hydrocarbons. Piperylene and isoprene were not hydrogenated on Zn at normal pressure and temperature up to 140° [6]. Piperylene was not hydrogenated either with an initial hydrogen pressure of 50 atm at 100°. At 80 atm, the degree of unsaturation of the catalyzate fell by 15%, at 100 atm, by 28%, and at 100 atm and 150° it fell to a half, which corresponds to complete hydrogenation of one double bond.

Thus, hydrogenation of zinc makes it possible to discriminate between the double bond in styrene or a conjugated double bond and an unactivated ethylene bond.

Hydrogenation of the Acetylene Bond. The triple bonds in acetylene, vinylacetylene, isopropenylacetylene, dimethylethynylcarbinol, and tolane [6] were selectively hydrogenated to double bonds on Zn at normal pressure. The reaction did not occur below 50-65°. Hydrogenation of the acetylene bond in dimethylvinylethynylcarbinol and 2-butyne-1,4-diol could be achieved under pressure (90-100 atm) at 80-130°. Thus, Zn catalyzes the hydrogenation of the acetylene bond in compounds with various structures. The reaction proceeds under more drastic conditions than on Ni.

Reduction of the Carbonyl Group. The reduction of aldehydes and ketones [7] on Zn began at 50-60° and normal pressure, i.e., approximately under the same conditions as on skeletal nickel. α,β-Unsaturated aldehydes

and ketones were selectively reduced to the corresponding unsaturated alcohols [8]. Methyl cyclopropyl ketone was also reduced at the C = O group only [4]. It should be noted that zinc did not always have a selective action. Thus, in the reduction of 2-methyl-2-hepten-6-one, in which the C = C bond is distant from the C = O group, Zn did not have a selective action; the C = C bond was mainly hydrogenated. The selectivity of the reduction of α,β-unsaturated aldehydes and ketones began to fall above 60-80° and the double bond content of the catalyzate fell rapidly [8]. It may be assumed that these anomalies are connected with peculiarities in the structure of the compounds reduced (for example, the absence of conjugation of the bonds in the molecule), with the adsorption displacement of some groups of atoms by others, or with a change in the catalysis mechanism under the changed conditions.

Generalization of the results obtained shows the peculiarity of the catalytic action of Zn in hydrogenation and reduction. Zinc does not catalyze the hydrogenation of olefins, while the hydrogenation of an ethylene bond activated by a phenyl group or a conjugated double bond is accelerated only at elevated temperatures or under pressure. Zn catalyzes the selective hydrogenation of an acetylene to an ethylene bond and, in particular, accelerates the reduction of the C = O group of aldehydes and ketones. The results obtained agree with the calculated values of the energy barriers of these reactions on zinc. Thus, the different sequence of the hydrogenation of bonds on Zn as compared with other metallic catalysts can also be explained by the formation of an intermediate complex.

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* Original Russian translation. See C. B. Translation.

ESTERS OF ETHYL-β-CHLOROVINYLPHOSPHINIC ACID

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(Presented by Academician A. E. Arbuzov, November 9, 1959)

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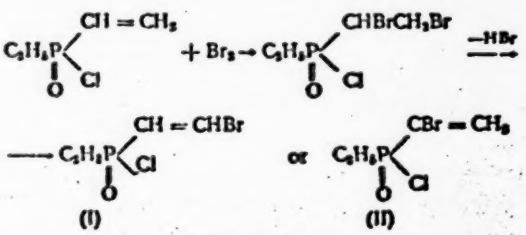
Original article submitted November 4, 1959

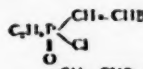
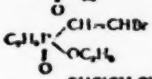
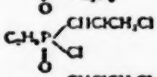
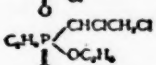
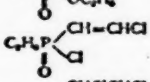
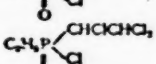
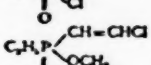
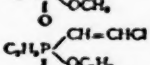
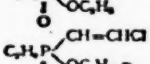
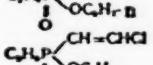
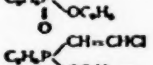
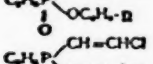
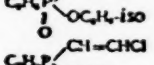
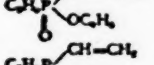
We recently reported the synthesis and some properties of derivatives of ethylvinylphosphinic acid [1]. In particular, it was reported that ethylvinylphosphinic chloride adds bromine, which qualitatively demonstrates the unsaturation of the vinyl group. However, on turning to quantitative measurement, we found that the increase in weight of the reaction product from ethylvinylphosphinic chloride and an equimolecular amount of bromine was approximately half of the calculated value. The molecular refraction found for the main fraction obtained by slow vacuum distillation of the product was close to that calculated for ethyl-β-bromovinylphosphinic chloride. According to analysis and molecular refraction, the ethyl ester obtained by the reaction of the product with ethanol in absolute ether in the presence of pyridine corresponded to ethyl ethyl-β-bromovinylphosphinate.

We consider that the bromination yielded ethyl-α,β-dibromoethylphosphinic chloride, but the latter is an unstable product and even after removal of the light fractions under vacuum at 50°, hydrogen bromide was eliminated with the formation of ethyl-β-bromovinylphosphinic chloride.



Although we leave the problem of the choice of the structure open, we prefer the first variant with the halogen atom at the β-carbon atom as in this case both steric and thermodynamic factors should make the molecule more stable. The chlorination of ethylvinylphosphinic chloride was studied more carefully. Contrary to what was stated above, the chlorination product, namely ethyl-α,β-dichloroethylphosphinic chloride, was found to be stable and distilled in vacuum without any signs of decomposition. Nonetheless, the tendency for the elimination of hydrogen chloride was still expressed by the high (almost quantitative) yield of ethyl-β-chlorovinylphosphinic chloride from the catalytic dehydrochlorination of ethyl-α,β-dichloroethylphosphinic chloride over a mixture of fired barium carbonate and activated charcoal at 330-350°.

Esters of ethyl-β-chlorovinylphosphinic acid were synthesized by the generally accepted method, i.e., by the reaction of the acid chloride with appropriate alcohols in absolute ether in the presence of an organic base (pyridine). They were all colorless, mobile liquids with a very weak smell, which were immiscible with water (with the exception of the methyl and ethyl esters).

Products	Temp., C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	P, % found	P, % calc.	Halogen, % found	Halogen, % calc.	Yield, %
	108—110/10	1,5260	1,6470	40,60	41,30	—	—	—	—	—
	97,5—98/10	1,4800	1,3760	47,11	46,95	13,45	13,62	34,91	35,20	40
	132—133/10	1,5100	1,4290	43,85	43,74	14,05	14,76	50,98	50,80	82
	105—107/3	1,4765	1,2410	49,83	49,39	—	—	32,00	32,50	30
	92—94/10	1,4935	1,3080	38,48	38,41	17,70	17,88	40,68	41,00	85
	135/10	1,5220	1,5190	48,91	48,61	12,60	12,70	57,60	58,20	22
	82—86/12	1,4650	1,1870	39,27	39,43	—	—	21,38	21,00	51
	85—89/10	1,4625	1,1260	44,66	44,05	—	—	19,86	19,42	63
	106—112/12	1,4600	1,1100	48,45	48,67	—	—	18,15	18,00	44
	93—94/3	1,4725	1,1360	48,03	48,20	—	—	17,80	18,20	73
	112—115/11	1,4600	1,0760	53,60	53,29	—	—	16,42	16,80	55
	103—106/12	1,4590	1,0870	52,95	53,29	—	—	17,00	16,80	41
	122—132/3	1,5305	1,1900	59,41	58,92	—	—	15,60	15,30	38
	114—115/3	1,5240	1,1140	53,88	54,06	15,54	15,74	—	—	35

As was to be expected [2], subsequent chlorination of ethyl-β-chlorovinylphosphinic chloride was difficult. Thus, after chlorination of 39 g of the latter for 3 hr, the bulk of the starting material was recovered from the reaction mixture, and ethyl-α,β,β-trichloroethylphosphonic chloride was isolated in only 22% yield. The constants of all the products obtained are given in the table.

A communication of some derivatives of β-chlorovinylphosphinic acid [3] contained no data on their polymerization. At the same time it seemed interesting to study the polymerization tendency of a vinyl group attached to an organophosphorous radical at one end and a halogen atom, in particular, chlorine, at the other and to compare these data with results obtained in the polymerization of ethylvinylphosphinic esters. Of the saturated esters, we investigated the methyl, ethyl, and butyl esters of ethyl-β-chlorovinyl- and the ethyl ester of ethyl-β-bromovinylphosphinic acid. Polymerization was carried out in sealed ampoules in the presence of 2% of benzoyl peroxide at 100-150°.

However, after prolonged heating (for 10 days) there was no appreciable change in viscosity of the products while, as was reported previously, esters of ethylvinylphosphinic acid polymerize under the same conditions to give viscous, sirupy masses and even lose their fluidity (at room temperature). From what has been said, it can be concluded that the peroxide polymerization of saturated esters of vinylphosphinic acid is hampered by the introduction of a halogen into the β-position. We are inclined to think that this is because of additional shielding of the double bond by the halogen atom.

A different picture was expected and was actually obtained in the polymerization of allyl esters of ethylvinyl- and ethyl-β-chlorovinylphosphinic acids. The investigations of Toy and Cooper [4] and of one of the present authors and Kukhtin [5] showed that the rate of polymerization of esters of phosphorus acids increase with the introduction of electronegative groups. In accordance with this, in the polymerization of these allyl esters with 2% of benzoyl peroxide, azoisobutyronitrile (parafor), or diazoaminobenzene, in the first two cases there was a sharp increase in the rate of polymerization of allyl ethyl-β-chloroethylphosphinate. While this ester was polymerized to a waxy mass even after 30 minutes at 40°, allyl ethylvinylphosphinate retained its original consistency after being heated for 4 hr at 40° and only formed a waxy mass when heated at 80° for 1 hr. The opposite result was obtained with initiation by diazoaminobenzene. When allyl ethylvinylphosphinic acid was heated for 10 hr (4 hr at 40° and 6 hr at 80°), the contents of the ampoule lost their fluidity; with allyl ethyl-β-chlorovinylphosphinate there was only an insignificant increase in viscosity. This phenomenon requires further investigation.

EXPERIMENTAL

Ethyl-α,β-dichloroethylphosphinic Chloride (I). A stream of chlorine was passed into vigorously stirred ethylvinylphosphinic chloride (80 g), cooled to −10°, at such a rate that the temperature of the reaction mass did not rise above +5°. The reaction was considered complete when the temperature no longer rose when cooling was stopped. The increase in weight of the flask contents was 50 g. The crude product was poured into an Arbuzov flask, the excess chlorine removed under reduced pressure, and the product vacuum distilled. We obtained 100 g of substance (I).

Ethyl-β-chlorovinylphosphinic Chloride (II). Substance (I) (75 g) was passed through a quartz tube filled with a layer of barium carbonate and then a layer of activated charcoal. The temperature inside the tubular furnace was kept within the limits of 330-350°. After distillation on a 25-cm pear fractionating column, a total of 50 g of substance (II) was isolated.

Allyl ethyl-β-chlorovinylphosphinate (III). A mixture of 400 ml of absolute ether, 11 g of allyl alcohol, and 14 g of pyridine was cooled to −10°. With vigorous stirring, 31 g of (II) was added dropwise from a dropping funnel. After the addition, the mixture was heated until the ether boiled, kept at this temperature for 2 hr, cooled and filtered free from pyridine hydrochloride. However, traces of pyridine hydrochloride were detected during distillation, and therefore, after the first distillation, the product was treated with an equal volume of cold 5% soda solution and then an equal volume of distilled water. Distillation of the lower layer yielded 20 g of (III).

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* Original Russian pagination. See C. B. Translation.

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CATALYTIC HYDROGENATION OF FURAN COMPOUNDS UNDER PRESSURE IN A FLOW SYSTEM

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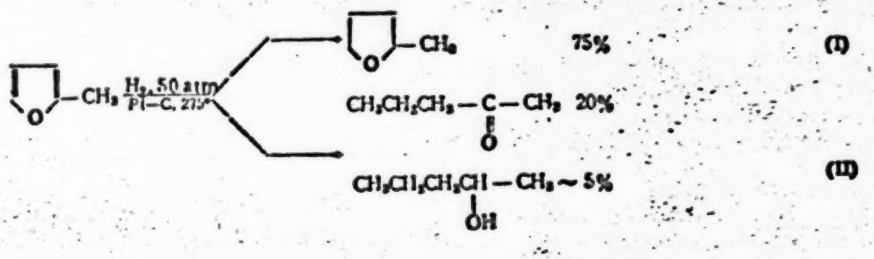
In the present work we present the results of investigating the hydrogenation of various furan compounds in a flow system at elevated hydrogen pressures on Pt–C and skeletal Ni–Zn and Ni–Al catalysts. A comparison of these results with experimental data obtained previously in the hydrogenation of furan derivatives in the vapor phase at normal pressure makes it possible to determine the effect of pressure on the capacity of the furan ring for hydrogenation to a tetrahydrofuran ring, or hydrogenolysis, and on the sequence and selectivity of the reduction of different unsaturated bonds in furan compounds.

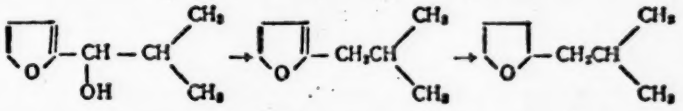
1. As is known [1], hydrogenation of sylvan on Pt–C at normal pressure and 275° leads to complete hydrogenolysis of the furan ring with the formation of methyl propyl ketone (reaction II); tetrahydrosylvan is not formed under these conditions. A completely different reaction course is observed in the hydrogenation of sylvan on Pt–C in a flow system at the same temperature, but under a hydrogen pressure of 50 atm. In this case the main reaction is the hydrogenation of sylvan to tetrahydrosylvan (reaction I), and hydrogenolysis of the furan ring occurs to a much lesser extent (about 25%).



2. We recently found [2] that in the hydrogenation of 2-methyl-5-acetylfuran on Pt–C at normal pressure, the primary reaction is mainly hydrogenolysis of the ring at the C–O bond adjacent to the carbonyl group. The 2,5-heptanedione thus formed cyclizes with the liberation of water to form 1-methyl-1-cyclohexen-3-one, which is then converted either into 3-methylcyclohexanone or m-cresol, depending on the temperature. Under these conditions, the primary reduction of the carbonyl group with subsequent hydrogenation and hydrogenolysis of the 2-methyl5-ethylfuran formed is a secondary process (about 20%). However, this process becomes practically the sole reaction in the hydrogenation of 2-methyl-5-acetylfuran on Pt–C at 230-250° and a hydrogen pressure of 50 atm.

heptanol-3 heptanone-3 heptanol-2 heptanone-2

3. In hydrogenation on Pt–C under the same conditions (250°, 50 atm), like the carbonyl group, the hydroxyl group in alkylfurylcarbinols is reduced before the furan ring is hydrogenated. For example, hydrogenation of isopropylfurylcarbinol gives a catalyzate containing about 30% of α-isobutylfuran and about 50% of α-isobutyltetrahydrofuran.



4. We studied the properties of skeletal Ni–Zn catalyst, in particular, in the vapor-phase hydrogenation of sylvan at normal pressure. Over a wide range of temperatures (150-300°), the sylvan underwent hydrogenolysis (70-75% at 150° and quantitatively at 270-300°). A small amount of tetrahydrosylvan was formed at low temperatures (not more than 20% at 150°). The use of elevated pressure in the hydrogenation of sylvan on skeletal Ni–Zn promoted hydrogenation of the multiple bonds in the furan ring and suppressed hydrogenolysis. However, this effect was less than on a platinum catalyst. At 250-260° and a hydrogen pressure of 50 atm, on a skeletal Ni–Zn catalyst, sylvan formed 35-40% of tetrahydrosylvan, 20-25% of 2-pentanone, and about 40% of 2-pentanol.

5. As we showed previously [3], in contrast to other nickel catalysts, skeletal Ni–Al catalyst has the peculiar property of promoting so-called "conjugated" hydrogenolysis of the furan ring during hydrogenation in a flow system at normal pressure. Even at 235-250°, the furan ring in α-alkylfurans is cleaved completely with the formation of three types of ketone, namely 2-alkanones, 3-alkanones, and 4-alkanones. α-Alkyltetrahydrofurans are not formed at this temperature. In this case also a rise in pressure substantially changes the direction of hydrogenation of the furan ring. Thus, as a result of hydrogenation of sylvan in a flow system at 270° and a hydrogen pressure of 50 atm, in the presence of an Ni–Al catalyst, we obtained about 50% of tetrahydrosylvan, 45% of aliphatic ketones and alcohols (butanol-2, methyl ethyl ketone, and methyl propyl ketone), and about 5% of n-pentane.

Thus, in all cases, increasing the hydrogen pressure in hydrogenation in a flow system promoted hydrogenation of the multiple bonds in the furan ring. This effect appeared to the greatest extent in reactions on platinized charcoal and to the least extent on nickel catalysts (skeletal Ni–Zn and Ni–Al). A rise in pressure also resulted in the fact that on Pt–C, the reduction of hydroxyl and carbonyl groups before hydrogenation of the furan ring became the main or even the sole primary reaction in the hydrogenation of alkylfurylcarbinols and alkyl furyl ketones.

EXPERIMENTAL

Catalysts. Platinized charcoal containing 10% of Pt was prepared by impregnating birchwood activated charcoal with chloroplatinic acid solution and then reducing the material with hydrogen in a reaction tube at 250-320°. Skeletal Ni–Zn and Ni–Al catalysts were prepared by incomplete removal of aluminum or zinc from alloys of these metals with nickel by treatment of lumps of the alloy with sodium hydroxide solution. Removal of the zinc required concentrated alkali and prolonged heating, while 10% NaOH solution was used for dissolving part of the aluminum from the alloy with nickel.

Starting Materials. Pure sylvan was isolated from the technical product by distillation on a column and had b.p. 62-64°(750); $n^{23}D$ 1.4320; d^{23}_4 0.9120. 2-Methyl-5-acetylfuran was obtained by acetylation of sylvan with acetic anhydride in the presence of phosphoric acid and had b.p. 68-69° (7); $n^{20}D$ 1.5095; d^{20}_4 1.0655. The yield was 45% of theoretical.

Isopropylfurylcarbinol was synthesized in 70% yield by the Grignard reaction from furfural and isopropyl bromide; it had b.p. 66-68° (5); $n^{19}D$ 1.4791; d^{20}_4 1.0297.

Experimental Conditions. The hydrogenation of sylvan, 2-methyl-5-acetylfuran, and isopropylfurylcarbinol on Pt–C and skeletal Ni–Zn and Ni–Al was carried out in a flow apparatus [4] at 230-275° and a hydrogen pressure of 50 atm. The reaction products were distilled on an efficient column. The substances obtained had the following properties.

Tetrahydrosylvan: b.p. 79-79.2° (747); $n^{22}D$ 1.4060; d^{20}_4 0.8582.

2-Pentanone: b.p. 100-102° (750); $n^{22}D$ 1.3912; d^{20}_4 0.8081; semicarbazone: m.p. 110°.

2-Pentanol: b.p. 118-119° (750); $n^{20}D$ 1.4060; d^{20}_4 0.8097.

2-Methyl-5-ethyltetrahydrofuran: b.p. 116.5-117° (742); $n^{22}D$ 1.4130; d^{20}_4 0.8403.

α-Isobutylfuran: b.p. 128-128.5 (750); $n^{20}D$ 1.4415; d^{20}_4 0.8785.

α-Isobutyltetrahydrofuran: b.p. 149-150° (755); $n^{22}D$ 1.4265; d^{20}_4 0.8484.

The tetrahydrosylvan and methyl ethyl ketone obtained by hydrogenation of sylvan on skeletal Ni–Al were contained in a fraction with b.p. 78-80°. The amounts of these compounds in the fraction were determined from the refractive index.

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SYNTHESES AND ANTIMICROBIAL PROPERTIES OF SOME ARYL ESTERS OF METHANE- AND ETHANETHIOSULFONIC ACID

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(Presented by Academician M. L. Kabachnik, December 29, 1959)

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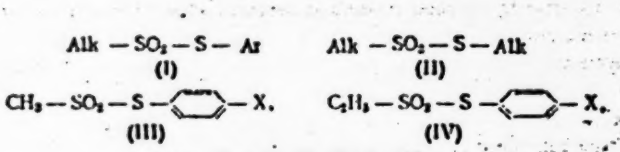
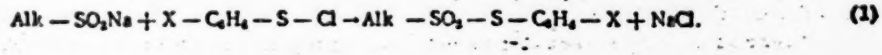
Up to now no aromatic esters of alkanethiosulfonic acids (I) have been described in the literature. Nonetheless, they are of practical interest as related compounds (II) frequently have a high antimicrobial activity, especially against phytopathogenic bacteria and fungi and also show plant growth stimulating properties [1].

For this reason, in the present work we decided to synthesize the first representatives of this group of compounds, namely, aryl esters of methane- and ethanethiosulfonic acids (III) and (IV), and to study their antimicrobial properties.



where X = H, Cl, CH_3O, NO_2.

We prepared the esters (I) by the reaction of the sodium salts of alkanesulfinic acids with sulfenyl chlorides according to the reaction



(1)

The sulfinates required were prepared by a known procedure [2], by conversion of the corresponding sulfonyl chlorides into the zinc salts by the action of zinc dust, and then treatment of these with sodium carbonate gave the sodium salts. The latter were dried carefully in vacuum before use; in the case of the hygroscopic sodium methanesulfinate, the necessary measures were taken to prevent access of moisture to the reaction mixture in the preparation of the esters (the salt was ground under a layer of absolute carbon tetrachloride, etc.). The use of silver sulfinates instead of the sodium salts had no appreciable effect, especially considering the loss of products during the conversion of the sodium into silver salts; for this reason we did not use silver salts after the first experiment.

Arenesulfenyl chlorides were obtained by the usual method [3-5], i.e., by the action of gaseous chlorine on solutions of thiophenols of disulfides in absolute ether or carbon tetrachloride. When thiophenols were used for this purpose, solutions of the latter in carbon tetrachloride were added with cooling to carbon tetrachloride containing an equimolar amount of chlorine and then the solvent was removed and the residue vacuum distilled.

We isolated benzenesulfenyl and p-chlorobenzenesulfenyl chlorides in a pure state; p-methoxybenzenesulfenyl chloride was obtained by an analogous procedure in the form of a reddish brown, oily liquid, which could

TABLE 1

Aryl Esters of Methane- and Ethanethiosulfonic Acids Alk–SO_2–S–Ar

Alkyl	Aryl	M.p., °C	Sulfur content, %		Yield, % of theoret.
			calc.	found	
CH_3	C_6H_5	85—86	34,06	34,12; 34,18	56,7
	p-ClC_6H_4	102—103	28,80	28,62; 28,96	46,1
	p-$CH_3OC_6H_4$	78—79	29,38	29,33; 29,46	50,0
	p-$NO_2C_6H_4$	148—149	27,49	27,35; 27,45	48,3
C_2H_5	C_6H_5	52	31,70	31,94; 31,90	40,9
	p-ClC_6H_4	55—56	27,09	27,15; 27,21	49,3
	p-$CH_3OC_6H_4$	38—39	27,60	27,45; 27,58	52,5
	p-$NO_2C_6H_4$	85	25,93	25,80	46,8

• The ester yields could be increased by the extraction of further amounts of these compounds from the mother solution.

not be vacuum distilled at a residual pressure of 10^{-2} mm Hg, and this compelled us to use it without additional purification, directly after removal of the carbon tetrachloride in vacuum. p-Nitrobenzenesulfenyl chloride was obtained by the action of gaseous chlorine on an ether suspension of p,p'-dinitrodiphenyl disulfide with subsequent removal of the excess chlorine and isolation of the crystalline product; this sulfenyl chloride was not purified further before use either.

Our attempts to prepare p-acetylaminobenzenesulfenyl chloride have not yet been successful; the action of gaseous chlorine on p,p'diacetyldiaminodiphenyl disulfide, like the action of chlorine on p-acetylaminothiophenol, gave insignificant yields of very impure sulfenyl chloride; the use of the latter for the synthesis of esters made it impossible to isolate the final products in a pure state. As is known [6], the action of bromine on the same disulfide leads to similar results. The esters were prepared in absolute benzene or carbon tetrachloride with the simultaneous introduction of the sulfinate and the sulfenyl chloride. The reaction first proceeded extremely vigorously with great evolution of heat; the colored solution was rapidly decolorized. The reaction mixture was then heated on a water bath for 2-3 hr and filtered free from the salt precipitate. The solvent was removed in vacuum and the residue, which crystallized when cooled in a mixture of ice and salt, was purified to constant melting point by recrystallization from alcohol. Even very slight overheating and also prolonged heating during distillation of the solvent from the sulfenyl chlorides and during its removal after the formation of the final product had a considerable effect on the purity of the latter and often led to the formation of uncrystallizable residues, evidently as a result of partial decomposition of the sulfenyl chlorides. When an excess of sulfinates over sulfenyl chlorides (1.3:1.0 in moles) was used, the yields of esters and the purity of the latter increased noticeably. The latter was especially important where the sulfenyl chlorides used were not in a pure state, as the need for repeated purification of the final products sharply reduced their yields. The esters we obtained are given in Table 1.

All these compounds were colorless, crystalline substances and only the p-nitrophenyl esters had a pale straw color. They were very soluble in benzene, alcohol, ether, acetone, and other organic solvents and very sparingly soluble in water.

The results of studying the antimicrobial activity of these compounds, which are given in Table 2, showed• that aryl esters of methane- and ethanethiosulfonic acids differ from the esters (II) in their antimicrobial properties; they had no action on gram-negative bacteria, were slightly more active than alkyl esters of alkanethiosulfonic acids with respect to gram-positive bacteria (Staphylococcus aureus), and were surpassed by them in activity against Mycobacterium B_3. The aryl esters of methane- and ethanethiosulfonic acids differed little from esters (II) with respect to action against various fungi; they were no less, and often more, active than the latter against Penicillium and Mucor, showed a higher activity against Fusarium and Saccar. ellipsoid, and had a weaker action on Aspergillus and, in particular, Rhizopus.

• The antimicrobial properties of the thiosulfonic esters were studied in the D. K. Zabolotnii Institute of Microbiology, Academy of Sciences, Ukr. SSR; we would like to thank V. G. Drobot'ko, B. E. Aizenman, and S. I. Zelepukhe for carrying out these investigations.

TABLE 2

Antimicrobial Activity of Aryl Esters of Methane- and Ethanethiosulfonic Acids (activity in dilutions in thousands*) Alk–SO_2–S–Ar

Alkyl	Aryl	Form of microorganism									
		Staphylococcus aureus	B. Coli	Mycobacterium B.	Penicillium	Aspergillus	Fusarium	Rhizopus	Mucor	Saccar. ellipsoid	Candida albicans
CH_3	C_6H_5	—	—	—	—	—	10	—	—	50	—
	p-ClC_6H_4	500	—	10	50	10	250	10	50	500	250
	p-$CH_3OC_6H_4$	10	—	50	50	—	250	50	10	50	50
	p-$NO_2C_6H_4$	500	—	—	10	—	50	—	50	500	500
C_2H_5	C_6H_5	500	—	50	50	50	500	10	10	50	50
	p-ClC_6H_4	500	—	50	250	50	250	50	250	500	500
	p-$CH_3OC_6H_4$	50	—	50	250	10	250	10	50	250	50
	p-$NO_2C_6H_4$	250	—	10	10	—	50	—	50	500	500

* A line denotes the absence of activity.

It should be noted that the esters of methanethiosulfonic acid given in Table 2 were less active than analogous esters of ethanethiosulfonic acid with respect to bacteria and fungi. Phehyl methanethiosulfonate showed no activity at all against the forms of bacteria tested and was almost inactive against the forms of fungus tested.

The aryl esters of methane- and ethanethiosulfonic acids were more interesting for their action on phytopathogenic fungi.

A study of the fungicidal activity of these compounds* carried out in the Ya. V. Samoilov Scientific Institute of Fertilizers and Insectofungicides (NIUIF) showed that some of them were highly active fungicides and in experiments in vitro they showed a fungistatic action against many fungi which, in many cases, exceeded that of such fungicides as Zineb and Captan (at the same concentrations) and at a higher concentration they gave better results than Figone.

For this reason we consider that aryl esters of alkanethiosulfonic acids are of great interest for further investigation; we are continuing to synthesize these compounds and study their antimicrobial activity.

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* We would like to thank N. N. Mel'nikov, K. A. Gar, and their co-workers for studying the fungicidal activity of the thiosulfonic esters.

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ESTERS OF UNSATURATED PHOSPHINOUS ACIDS

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Esters of unsaturated phsophinous acids (which have not been described in the literature up to now) combine in one molecule an unsaturated grouping and a trivalent phosphorous atom, connected by a C–P bond. This causes the high reactivity of these compounds and the variety of their chemical conversions offer the possibility of their use for the synthesis of various organophosphorus compounds, including polymers.

An investigation of the reactivity of esters of unsaturated phosphinous acids is also interesting in connection with the study of the intereffect of unsaturated carbon–carbon bonds and a trivalent phosphorus atom, and the determination of the character of orientation in π–p conjugated systems containing phosphorus.

In the present work we describe the synthesis and some conversions of derivatives of vinyl-, ethynyl-, and p-vinylphenylphosphinous acids.

The dibutyl esters of vinyl- and ethynylphosphinous acids (I and II, see the table) were obtained by a method developed previously [1], namely, the reaction of appropriate organomagnesium compounds with dibutyl chlorophosphite in tetrahydrofuran.

$$RMgX + ClP(OR')_2 \xrightarrow{-60^\circ} RP(OR')_2 + MgXCl.$$

Similarly, from vinylmagnesium bromide and phenylbutoxychlorophosphine (III) we synthesized the butyl ester of secondary vinylphenylphosphinous acid (IV). From p-vinylphenylmagnesium chloride and diethylchlorophosphite we obtained the styrene derivative (V). As esters of unsaturated phosphinous acids were found to be strong complex formers, to isolate them from the reaction mixture it was necessary to use substances which displace the phosphinous esters formed from the complex compounds with magnesium halides. As this complex former we used pyridine, which was shown by E. L. Gefter [2] to give good results in the isolation of phenyldichlorophosphine from the complex with aluminum chloride. The relative resistance of the esters of unsaturated phosphinous acids to hydrolysis also made it possible to use washing with water or sodium bicarbonate solution for decomposing the complex compounds with magnesium halides.

The substances obtained were readily oxidized in air but apparently less vigorously than the corresponding alkylphosphinous esters as, in contrast to the alkyl derivatives, esters of unsaturated phosphinous acids did not "fume" when deposited on cotton wool or paper. We examined some reactions of esters of vinyl- and ethynylphosphinous acids (I) and (II), which confirmed the structure of these compounds as unsaturated derivatives of trivalent phosphorus.

It was previously shown that the hydrolysis of full esters of phosphinous acids leads to the corresponding acid esters [3]. Similarly, the butyl esters of vinyl- and ethynylphosphinous acids (I) and (II) reacted with the theoretical amount of acidified water in dioxane to give the readily polymerizable monobutyl esters of these acids (VI) and (VII).

The trivalent state of the phosphorus in the dibutyl ester of vinylphosphinous acid (I) was also demonstrated by the addition of sulfur and the Arbuzov rearrangement with methyl iodide, as a result of which we obtained the dibutyl ester of vinylthiophosphinic acid (VIII) and the butyl ester of vinylmethylphosphinic acid (IX), respectively. It should be noted that in an attempt to achieve the Arbuzov rearrangement of the dibutyl ester of vinylphosphinous acid (I) by boiling in excess methyl iodide, mainly polymeric products were isolated. Polymerization also occurred when the reaction was carried out in acetonitrile at 0°. A positive result was obtained only when ligroin was used as the solvent. However, the process was very slow in this case and quite drastic conditions were required to carry out the reaction (100-110°, 4 hr).

As a dienophile, the dibutyl ester of vinylphosphinous acid (I) underwent diene synthesis with cyclopentadiene to form the corresponding adduct, namely the dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-phosphinous acid (X). The latter contained a trivalent phosphorus atom in the molecule, as was demonstrated by the addition of sulfur. The yields, constants, and analytical data for all the compounds obtained are given in the table.

EXPERIMENTAL

All operations were carried out in an atmosphere of purified nitrogen and the solvents were dried carefully.

Dibutyl ester of vinylphosphinous acid (I). A solution of vinylmagnesium bromide [4] (0.65 g-at of magnesium, 0.67 mole of vinyl bromide, and 500 ml of tetrahydrofuran) was added dropwise to 0.60 mole of dibutyl chlorophosphite in 200 ml of tetrahydrofuran with vigorous stirring and a reaction mixture temperature of −60°. After the addition, the tetrahydrofuran was removed in vacuum; to the residue was added 300 ml of ligroin and 1.3 mole of pyridine, the precipitate removed and washed with ligroin (5 x 100 ml), the solvent evaporated, and the residue vacuum distilled in the presence of hydroquinone.

The dibutyl ester of ethynylphosphinous acid (II) was synthesized analogously from ethynylmagnesium bromide [5] (from 0.12 mole of ethyl bromide, 0.12 g-at of magnesium and acetylene in 80 ml of tetrahydrofuran) and 0.01 mole of dibutyl chlorophosphite in 50 ml of tetrahydrofuran.

Phenylbutoxychlorophosphine (III). A mixture of 0.3 mole of butyl alcohol and 0.3 mole of diethylaniline in 50 ml of ligroin was added dropwise with stirring to 0.3 mole of phenyldichlorophosphine [2] in 300 ml of ligroin at −30°, the mixture stirred for 1 hr, the precipitate removed and washed with ligroin, the solvent evaporated, and the residue vacuum distilled.

The butyl ester of vinylphenylphosphinous acid (IV) was synthesized similarly to the dibutyl ester of vinylphosphinous acid (I) by the reaction of vinylmagnesium bromide (0.12 mole of vinyl bromide, 0.11 g-at of magnesium, and 60 ml of tetrahydrofuran) with 0.10 mole of phenylbutoxychlorophosphine in 50 ml of tetrahydrofuran.

The diethyl ester of p-vinylphenylphosphinous acid (V) was obtained from p-vinylphenylmagnesium chloride [6] (0.06 mole of p-chlorostyrene, 0.06 g-at of magnesium, and 40 ml of tetrahydrofuran) and 0.06 mole of diethyl chlorophosphite in 40 ml of tetrahydrofuran. Sodium nitrite was used as a polymerization inhibitor.

Acid esters of vinyl- and ethynylphosphinous acids (VI) and (VII). A mixture of 0.03 mole of the appropriate full ester of the phosphinous acid (I) or (II), 0.033 mole of water, containing 0.4% sulfuric acid, and 10 ml of dioxane was left to stand at room temperature (40° in the case of the ethynyl derivative) for 30 min, the dioxane removed in vacuum, and the residue vacuum distilled in the presence of hydroquinone.

Dibutyl ester of vinylthiophosphinic acid (VIII). Sulfur (0.017 g-at) was added with stirring to 0.017 mole of the dibutyl ester of vinylphosphinous acid (I) in 15 ml of absolute ether at 0°. After the sulfur had dissolved, the ether was evaporated and the residue vacuum distilled.

Butyl ester of methylvinylphosphinic acid (IX). A mixture of 0.03 mole of the dibutyl ester of vinylphosphinous acid (I) and 0.09 mole of methyl iodide in 100 ml of ligroin was heated for 4 hr in an autoclave in the presence of hydroquinone at 100-110°. The solvent was then evaporated and the residue vacuuum distilled.

Dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-phosphinous acid (X). A mixture of 0.03 mole of the dibutyl ester of vinylphosphinous acid (I) and 0.015 mole of cyclopentadiene dimer was heated for 13 hr in a sealed tube in the presence of hydroquinone at 190-200°. The reaction mixture was fractionated in vacuum.

Dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-thiophosphinic acid (XI). Sulfur (0.0094 g-at) was added to 0.0094 mole of adduct (X) at room temperature. The reaction product was vacuum distilled.

Formula	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D		C, %		H, %		P, %		S (Cl), %	
					found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
I. $CH_2=CHP(OC_2H_5)_2$	71	49—51,5/2	1,4471	0,9039	60,39	60,04	58,7 58,6	58,8	10,5 10,5	10,4	15,0 15,1	15,2		
II. $CH\equiv C-P(OC_2H_5)_2$	74	58,8—60/2	1,4520	0,9289	58,73	58,50	59,0 59,3	59,4	9,6 9,6	9,5	15,2 15,5	15,3		
III. $C_6H_5P(OC_2H_5)Cl$	62	77—78/2	1,5352	1,1049	61,08		55,7 55,7	55,4	6,6 6,5	6,5	14,1 14,0	14,3	16,2 16,4	16,4
IV. $CH_2=CH(C_6H_5)POC_2H_5$	66,4	76—77/2	1,5310	0,9762	66,00		69,2 69,4	69,2	8,2 8,2	8,2	14,9 14,6	14,9		
V. $P-CH_2=CHC_6H_4P(OC_2H_5)_2$	33	96,5—97/2	1,5398	1,0251	68,61		63,9 64,2	64,3	7,6 7,8	7,6	13,9 14,0	13,8		
VI. $CH_2=CHPH(O)OC_2H_5$	92	50—51/2	1,4479	1,0040	39,50	39,40	48,7 48,6	48,6	9,1 8,9	8,8	20,8 20,8	20,9		
VII. $CH\equiv CPH(O)OC_2H_5$	78	65—66/1,5	1,4492	1,0322	38,00	37,66	49,4 49,3	49,3	7,6 7,5	7,6	21,1 20,9	21,2		
VIII. $CH_2=CH-P(S)(OC_2H_5)_2$	88,2	96,2—96,8/2,5	1,4730	0,9954	66,61	66,27	51,2 51,1	50,8	9,0 9,0	9,0	12,9 13,1	13,1	13,6 13,7	13,6
IX. $CH_2=CH(CH_2)P(O)OC_2H_5$	84	64—64,2/2	1,4452	0,9802	43,78	43,80	52,1 52,0	51,8	9,3 9,4	9,3	18,9 19,0	19,1		
X.	55,5	99,7—101/1,5	1,4792	0,9696	79,12	78,73	66,5 66,8	66,6	10,2 10,0	10,1	11,6 11,5	11,5		
XI.	63,5	139—139,2/2	1,4969	1,0423	84,87	84,96					10,0 10,1	10,2		

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INTERACTION OF FLUOROOLEFINS WITH HYDRAZOIC ACID AND THE REARRANGEMENT OF PERFLUOROALKENYL AZIDES

Academician I. L. Knunyants and É. G. Bykhovskaya

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April, 1960

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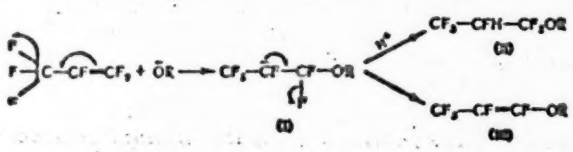
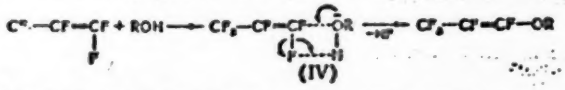
In reactions of various compounds with perfluoroolefins, together with addition at the multiple bond there also occurs replacement of fluorine atoms in the vinyl and, in some cases, the allyl position [1]. The addition and replacement processes are independent and are the result of conjugation of the bonds in φ-olefins. The initial act in the reaction is considered to be attack by an anion; the intermediate carbanion (I) is stabilized either by capture of a proton to form the saturated ether (II) or by elimination of a fluorine anion as a result of conjugation of the bonds in it to form a vinyl alkyl ether (III) [2].



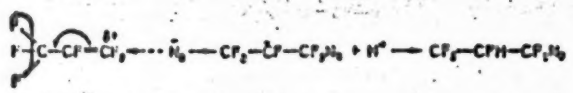
However, there is as much justification for the hypothesis that the electrophilic molecule of the fluoroolefin adds an undissociated molecule of the nucleophilic reagent due to the unshared pair of electrons with the formation of a four-membered transition complex (IV); the latter is stabilized by the formation of an intramolecular H. . .F hydrogen bond, which simultaneously facilitates the elimination of hydrogen fluoride with the formation of a vinyl-substitution product.



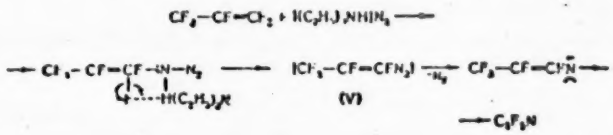
(IV)

Other experimental data on the addition of alcohols to φ-olefins are in good agreement with this treatment. Thus, the addition of ethyl alcohol to trifluorochloroethylene in the presence of sodium ethylate leads solely to trifluorochlorodiethyl ether, while passing trifluorochloroethylene through a suspension of Na ethylate in ether forms ethyl difluorochlorovinyl ether [3].

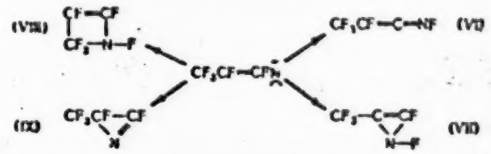
These rules are confirmed by the previously unstudied reaction of φ-olefins with hydrazoic acid. Thus, the reaction of φ-propylene and φ-isobutylene with a suspension of sodium azide in alcohol forms saturated β-monohydroperfluoropropyl and β-monohydroperfluoroisobutyl azides.



The formation of a very small amount of vinyl-substitution product was observed only in the case of φ-isobutylene. Replacement of the solvent (alcohol) by nonpolar symmetrical tetrachloroethane, in which the triethylammonium salt of hydrazoic acid is soluble, led to the formation of the vinyl-substitution product (V) in appreciable yield in the case of φ-propylene. Perfluoroalkenyl azides (vinyl-substitution products) were extremely unstable and spontaneously lost nitrogen at room temperature to form an "azacarbene," which then rearranged.



This rearrangement of the "azacarbene" may occur as a result of the transfer of fluorine to the nitrogen atom from the α-(VI), β-(VII), or γ-position (VIII), and also as a result of "pairing" of the electrons of the π-bond (IX).

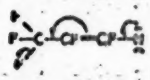


A colorless, gaseous compound with b.p. −17° was formed as a result of the reaction between φ-propylene and HN_3. The infrared spectrum was investigated in order to determine the structure of this compound. In the region of valence oscillations of double bonds, there was a broad intense band with a maximum at 1724 cm^{-1}. Substances containing cumulate bonds are known to have a high oscillation frequency. Thus, allene =C=C=C= has a very strong band at 1980 cm^{-1}. On this basis we can exclude structure (VI) from the examination. As is known, the characteristic frequencies of C=C and C=N are displaced toward the shortwave part of the spectrum as the number of fluorine atoms on the carbon atoms increases. Thus, we have the following frequencies: C_2H_4 $\nu_{C=C}$ 1626, $CH_2=CHF$ 1650, $CH_2=CF_2$ 1728, $CFH=CF_2$ 1788, $CF_2=CF_2$ 1872 cm^{-1}. In imino compounds containing no fluorine, the oscillation frequency of C=N− practically coincides with that of an olefin bond and is in the region of 1620-1680 cm^{-1}. In fluorine-containing compounds of this type, it increases sharply and in $CF_3N=CF_2$, for example, it reaches 1809 cm^{-1}. Haszeldine's data [4] show that in compounds containing the grouping −CF=CF− the oscillation frequency of =C=C= has an approximately constant value of 1733 cm^{-1}. The characteristic frequency of the double bond of the compound investigated is close to the frequency found in [4] for the olefin bond in the grouping −CF=CF−. Moreover, structure (VII) contains a =C=C= bond with only one fluorine atom on the carbon atoms and, according to available data, one would expect a considerably lower frequency for this double bond.

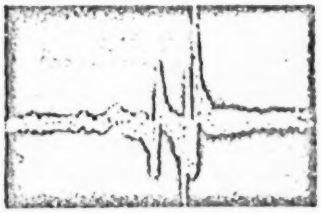
Thus, structures (VIII) and (IX) are most probable. However, structure (VIII) is more likely, due to the presence of another strong absorption at about 1000 cm^{-1}, which is apparently connected with oscillations of the N−F bond. This is also in accord with the nuclear magnetic resonance spectrum of this substance*. In actual fact, in contrast to all the other structures proposed, structure (VIII) has fluorine atoms in 4 nonequivalent positions, which shows in the form of four signals in the nuclear magnetic resonance spectrum. According to literature data, the lines observed are characteristic of the following fluorine-containing groups: =NF, $=CF_2$, =CF− (Fig. 1).

Thus, the data from nuclear magnetic resonance and infrared spectra show that the gaseous compound with b.p. −17° is perfluoroazacyclobutene-2 (structure VIII) and consequently, the "perfluoropropenyl azacarbene" is stabilized due to the transfer of a fluorine atom to the nitrogen from the γ-position.

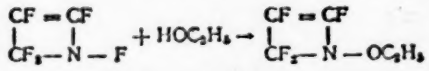
Like the normal allyl rearrangement, this process is the result of conjugation of the bonds in the "azacarbene."



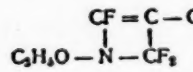
* The infrared spectra and the nuclear magnetic resonance spectrum were plotted by S. S. Dubov.



The fluorine atom on the nitrogen in perfluoroazacyclobutene is very labile; it is hydrolyzed by 1/10 N alkali in the cold and is replaced by an ethoxyl group in absolute alcohol at 10° to give 1-ethoxyazacyclobutene-2, a liquid with b.p. 96°.



Similar processes occur in the reaction of φ-isobutylene with sodium azide in alcohol. In this case, together with the main reaction product, β-monohydroperfluoroisobutyl azide, a small amount of a product with b.p. 112° was formed and this was 1-ethoxy-3-trifluoromethylazacyclobutene-2.



The structure of this compound was confirmed by the infrared spectrum, which was identical with that of compound (VIII). Consequently, perfluoroalkenyl azides are extremely unstable compounds, which spontaneously lose a molecule of nitrogen; evidently they cannot be isolated in the free state.

In contrast to them, β-monohydroperfluoroalkyl azides are stable, readily distillable liquids, which are unchanged when heated with water and with 1/10 N alkali. These results again confirm the fact that the formation of perfluoroalkenyl azides occurs as a result of replacement of the vinyl fluorine atom of φ-olefins and not as a result of the elimination of hydrogen fluoride from saturated monohydroperfluoroalkyl azides.

EXPERIMENTAL

Reaction of φ-Propylene with a Suspension of Sodium Azide in Alcohol. Into a three-necked flask with a stirrer and gas inlet and outlet tubes were placed 40 ml of ethyl alcohol and 3.3 g of activated sodium azide. Then dry φ-propylene (2.5 liters) was passed in with vigorous stirring at room temperature. The precipitate was removed and the filtrate distilled on a fractionating column. This yielded two fractions:

1) Monohydroperfluoropropyl azide as a colorless mobile liquid with b.p. 51°; d^{20}_4 1.4962; $n^{20}D$ 1.3100; MR_D found 24.86; calculated 24.64.

Found %: C 18.89; H 0.53; N 21.46; F 59.32 $C_3HF_6N_3$. Calculated %: C 18.65; H 0.52; N 21.76; F 59.06

2) Ethyl 2-monohydroperfluoropropyl ether with b.p. 64°; d^{20}_4 1.3050; $n^{20}D$ 1.2963 Literature data [4]: b.p. 64°; d^{20}_4 1.2990; $n^{20}D$ 1.2960.

Reaction of φ-Isobutylene with a Suspension of Sodium Azide in Alcohol. Perfluoroisobutylene (2.5 liters) was passed into a suspension of 6.5 g of sodium azide in ethyl alcohol, cooled in ice. Vigorous evolution of nitrogen was observed. The reaction mixture was left at room temperature until the evolution of nitrogen ceased. The sodium fluoride precipitate (F found, 43.5%; calculated, 45%) was removed and the reaction mixture distilled on a fractionating column. A fraction boiling at 71-76° was collected. This was washed carefully with water, dried with calcium chloride, and redistilled. Three products were isolated.

1) Ethyl 2-hydroperfluoroisobutyl ether as a colorless liquid with b.p. 82-83° (739 mm); d^{20}_4 1.3039; $n^{20}D$ 1.2940. It did not contain nitrogen. According to literature data [1], ethyl-2-hydroperfluoroisobutyl ether has b.p. 83.5-84°; d^{20}_4 1.4061; $n^{20}D$ 1.2950. 2) β-Monohydroperfluoroisobutyl azide (this could not be isolated in an analytically pure state as its boiling point was close to that of ethyl 2-hydroperfluoroisobutyl ether). The colorless liquid had b.p. 71° (739 mm); d^{22}_4 1.5840; $n^{22}D$ 1.3020.

Found %: C 20.20; H 0.91; F 61.60; N 14.25 $C_4HF_8N_3$. Calculated %: C 19.85; H 0.51; F 62.55; N 17.32

3) 1-Ethoxy-3-(trifluoromethyl)-perfluoroazacyclobutene-2. The colorless liquid with a pleasant, weak smell had b.p. 112°(740 mm) d^{22}_4 1.4350; $n^{22}D$ 1.3172; mol. weight found 214, calculated 221.

Found %: C 32.44; H 2.21; F 52.52; N 5.65 $C_6H_5F_6ON$. Calculated %: C 32.52; H 2.26; F 51.59; N 6.33

Reaction of Perfluoropropylene with Triethylammonium Azide. The dry propylene (2.5 liters) was passed into a solution of 14 g of triethylammonium azide in 80 ml of symmetrical tetrachloroethane at 0°. The reaction mixture was washed with dilute hydrochloric acid and water and dried with magnesium sulfate. The solution was placed in a Favorskii flask, the outlet of which was connected to an ampoule cooled in a dry ice–acetone mixture. Liquid (7 ml) was collected in the ampoule at a residual pressure of 50-30 mm. The liquid was transferred to a distillation flask with a condenser and an adapter, whose end was connected to an ampoule immersed in a cooling mixture. As soon as the liquid in the flask reached room temperature, the evolution of nitrogen began and a gaseous substance condensed in the ampoule. When the evolution of nitrogen ceased, the residue was distilled on a fractionating column. β-Monohydroperfluoropropyl azide was a colorless liquid with b.p. 51°; d^{25}_4 1.4267; $n^{25}D$ 1.3105; MR_D found 24.88; calculated 24.64.

Found % N 21.96; F 59.08 $C_3HF_5N_3$. Calculated % N 21.76; F 59.06

The gas collected in the ampoule had b.p. −17°. Mol. weight: found 143.2, calculated 145.

Found % F 65.77 $CF_2{-}CF{=}CF{-}N{-}F$. Calculated %: F 65.50

Hydrolysis of Perfluoroazacyclobutene-2. Into a jar fitted with a stopper with a tap were placed a 1/10 N solution of alkali and a sample of perfluoroazacyclobutene-2. The jar was evacuated and the ampoule with the sample broken; the mixture was left to stand for 30 min and then the excess alkali titrated and the fluorine content of the solution determined (12.87%).

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* Original Russian pagination. See C. B. Translation.

COLOR OF ARSENO COMPOUNDS AND THE DEVELOPMENT OF COLOR DURING POLYMERIZATION

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(Presented by Academician A. N. Nesmeyanov, October 13, 1959)

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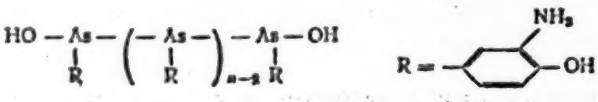
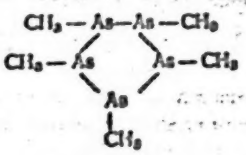
The intense yellow color of salvarsan was previously [1] explained by the presence of $-As=As-$ groups in its structure, similarly to the color of azo compounds, and it was even considered that this color confirmed the previously accepted structural formula. However, it has now been shown that salvarsan is a polymeric compound [2] with the structure



(I)

so that this explanation of the color naturally is incorrect. The actual reason for the color of salvarsan, its chromophoric group, is a chain of unsaturated arsenic atoms. Of the five valence electrons of As, three are used in the formation of the bonds shown in formula (I) while the remaining pair of electrons are involved in that interaction of the electronic systems of the atoms that we call "conjugation of the bonds" in the case of a chain of unsaturated carbon atoms. From this point of view, the salvarsan molecule, an unusual polyene, is colored in exactly the same way as compounds with quite a long chain of conjugated bonds (unsaturated carbon atoms). This point of view is confirmed by the following facts: Arsenomethane, which is an almost colorless liquid with b.p. 190°/15 mm, forms intensely colored polymers. Arsenomethane is known to be a cyclic compound (II), while the polymers have a linear structure [3] (I, R = CH_3).

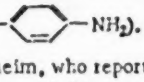


(II)

In this case there can hardly be any other explanation for the color of arsenomethane polymers as, apart from the chain of unsaturated arsenic atoms, the polymer molecule contains no chromophoric groups. Moreover, A. Michelis [4] observed that arsenobenzene forms resins (polymerizes) very readily. A sticky, yellow resin is obtained in this case [5]. Any other explanation of the color is difficult in this case also. In addition, the formation of chains of unsaturated atoms of other elements is known to lead to the formation of colored compounds. Thus, H_2S is colorless, while polysulfanes (for example, HS–S–S–S–S–H) have a yellow color. All that has been said conclusively

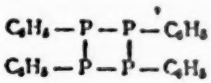
indicates that the chromophore of salvarsan is the chain of unsaturated As atoms. We consider that the determination of the actual reason for the color of salvarsan is of great importance for the determination of the structure of other arseno compounds. After the discovery of the chemotherapeutic activity of salvarsan by Ehrlich and Bertheim [1], a large number of investigators have synthesized "arseno compounds" of various types (all isomers of salvarsan and its homologs and analogs among heterocyclic and polycyclic compounds have been prepared). As a result, various arseno compounds have been described in the literature, which, however, have not been studied. We are unable to study all the arseno compounds described in the literature, the more so as these investigations are far from simple (the study of the structure of salvarsan required many years of tenacious work). The color of arseno compounds provides a good criterion for determining their structures: If the arseno compound is colored, it contains a chain of unsaturated As atoms and therefore is a polymer, while colorless arseno compounds, especially if they crystallize, are cyclic compounds with six- (as in the case of arsenobenzene [5]) or five-membered rings of arsenic atoms.

We present a few examples from the large number of arseno compounds investigated. 4,4'-Diaminoarsenobenzene was described by P. Ehrlich and A. Bertheim [6] as a yellow powder, which dissolved in dilute acids to form yellow solutions.

According to the ideas above, this compound is a polymer and as in the case of salvarsan, its chromophore is a chain of unsaturated, trivalent arsenic atoms (formula I, R = ). The polymeric nature of this compound is also indicated by the data of P. Ehrlich and A. Bertheim, who reported that low results were obtained when it was determined iodometrically, as in the case of salvarsan, and this is explained by the presence of terminal groups in the polymer molecule [2].

Novarsenol (neosalvarsan) is also a yellow powder, dissolving in water to form a yellow solution, which indicates its polymeric structure [formula I, R = $-C_6H_3(OH)(NHCH_2SO_2Na)$]. We previously [7] assigned a polymeric structure to novarsenol on the grounds that it is obtained under very mild conditions by the action of rongalite ($HOCH_2SO_2Na$) on a polymeric compound (salvarsan) and also on the basis of data on the diffusion of its solutions [8]. The yellow color of novarsenol is confirmation of the compound's polymeric structure.

Such arseno compounds as arsenobenzene, arsenotoluene, and arsenoanisole, which are colorless and crystallize readily, are cyclic compounds, containing a six-membered ring of As atoms [5]. The development of color on polymerization has also been observed in other cases where chains of unsaturated atoms are formed. Thus, W. Kuhen and W. Buchwald [9] observed that almost colorless phosphobenzene, to which they assigned the following cyclic structure on the basis of a cryoscopic determination of the molecular weight:



melted at 150.5° to form an intense yellow substance. Similarly, when arsenobenzene is fused, it polymerizes to form a sticky, yellow resin. It is extremely probable that the same occurs when "phosphobenzene" is fused and in any case, the yellow color of the melt conclusively indicates the formation of a chain of unsaturated, trivalent phosphorus atoms. In previous work [10] we showed that the so-called Schenck's phosphorus, which is obtained by heating a solution of yellow phosphorus in PBr_3, is actually a polymer, consisting of P atoms with $\equiv P-Br$ terminal groups, and not an adsorbate of PBr_3 on red phosphorus, as was considered. In our opinion, the color of Schenck's phosphorus (orange-red) is good confirmation of the structure we proposed.

In actual fact, in accordance with all that has been stated, the color of Schenck's phosphorus and probably that of other forms of red phosphorus may be explained by the formation of not just chains of trivalent P atoms, but a lattice of these atoms. We have the same in graphite, in which each carbon atom is firmly bound to only three nearest atoms (C—C = 1.42 A), while the bond with the fourth atom is incomparably weaker (C—C = 3.35 A). Thus, a graphite "molecule" is a plane of hexagons formed by unsaturated carbon atoms and this naturally leads to the possibility of "conjugation of bonds" in two dimensions, which also explains the absorption of all visible radiation by graphite. The crystal structure of diamond shows that all four valence electrons of the carbon atoms are used in the formation of identical bonds (the C—C distance equals 1.54 A in all cases) and therefore diamond is colorless. Thus, the color of true polyenes (for example, carotene), salvarsan, and other polymeric arseno compounds, and also polymeric compounds of phosphorus and graphite is caused by the same phenomenon, namely, the formation of chains or lattices of unsaturated atoms.

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* See C. B. translation.

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DIFFERENTIAL CONDUCTOMETRIC TITRATION OF A MIXTURE OF METHYLCHLORSILANES IN NONAQUEOUS SOLUTIONS

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In recent years, monomeric and polymeric organosilicon compounds and also various materials based on them have found wide practical application in science and industry, and in various new techniques. The main raw materials for their synthesis are alkyl (aryl) chlorosilanes, which are obtained by direct synthesis from alkyl (aryl) chlorides and metallic silicon [1].

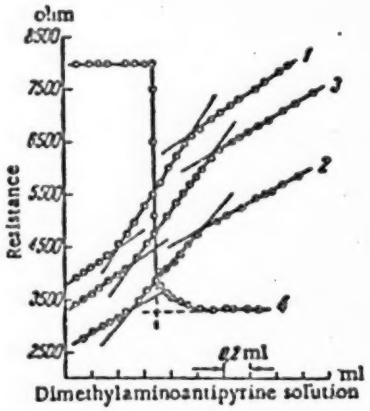

Fig. 1. Curves for the conductometric titration of binary mixtures of methylthiocyanosilanes with a 0.1 M benzene solution of dimethylaminoantipyrine in an acetonitrile–diethyl ether medium: 1) methyltrithiocyanosilane + dimethyldithiocyanosilane; 2) trimethylthiocyanosilane + dimethyldithiocyanosilane; 3) trimethylthiocyanosilane + methyltrithiocyanosilane; 4) curve for the replacement of chlorine atoms in alkylchlorosilanes by thiocyano groups.

However, up to the present no methods with sufficient accuracy and speed have been developed for the analysis of multicomponent mixtures of alkyl (aryl)chlorosilanes [2, 3]. The methods of analyzing alkylchlorosilanes based on their fractional distillation and subsequent determination of chlorine in the fraction obtained [4] and also the gas–liquid chromatographic [5], mass spectrometric [3], and Raman spectral methods [6] require complex apparatus, have been developed little, and therefore have not been introduced into practice. There are also other methods of analyzing alkyl (aryl)chlorosilanes [7-9], but they have only been applied to the determination of individual compounds.

We developed a new method of differential quantitative determination of individual methylchlorosilanes in binary and three-component mixtures, consisting of trimethylchlorosilane, dimethyldichlorosilane, and methyltrichlorosilane. The method is based on preliminary quantitative conversion of alkylchlorosilanes into alkylthiocyano derivatives by means of ammonium thiocyanate and subsequent conductometric titration of the alkylthiocyanosilanes in an acetonitrile–ether medium with a benzene solution of dimethylaminoantipyrine.

EXPERIMENTAL

The materials for our investigation were trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, and their binary and three-component mixtures. The starting methylchlorosilanes were purified and had physicochemical constants corresponding to literature data. Solutions of methylchlorosilanes in

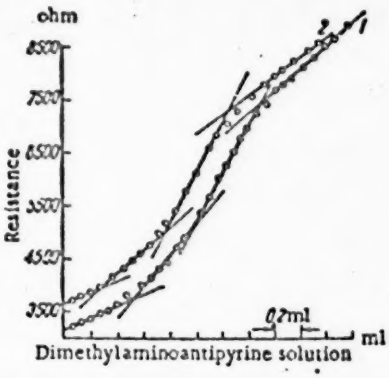

Fig. 2. Curves for the conductometric titration of three-component mixtures of methylthiocyanosilanes with a 0.1 M benzene solution of dimethylaminoantipyrine in an acetonitrile–diethyl ether medium: 1) trimethylthiocyanosilane + dimethyldithiocyanosilane + methyltrithiocyanosilane (in a ratio of 1 : 1 : 1); 2) trimethylthiocyanosilane + dimethyldithiocyanosilane + methyltrithiocyanosilane (in a ratio of 1 : 2 : 2).

dry benzene were prepared. For the titration we used a 0.1 M benzene solution of dimethylaminoantipyrine, prepared from an accurately weighed sample of reagent. We were the first to use dimethylaminoantipyrine as a titrant. The dimethylaminoantipyrine was recrystallized from water and dried to constant weight in a thermostat at 105°. Ammonium thiocyanate was prepared as a 0.3 M solution in acetonitrile. The titration was carried out in a closed cell with platinized platinum electrodes in the form of small plates (1 × 1 cm) sealed into the lid of the cell. The apparatus for conductometric titration consisted of the following parts: an R-38 slide-wire voltage bridge, a ZG-1 sound generator, and an INO-ZM null indicator instrument.

Determination Procedure. Into the conductometric titration cell was poured a mixture of solvents, consisting of 2 parts (by volume) of acetonitrile and 3 parts of diethyl ether. The mixture of solvents had sufficient electrical conductivity for the given titration and ensured that the products of the chemical reactions occurring were precipitated. Into the prepared mixture of solvents were poured benzene solutions of the methylchlorosilanes from a microburette and the solution titrated with ammonium thiocyanate.

An exchange reaction occurred between the methylchlorosilanes and ammonium thiocyanate according to the equation

$$(CH_3)_nSiCl_{4-n} + (4-n)\,NH_4SCN \rightarrow (CH_3)_nSi(SCN)_{4-n} + (4-n)\,NH_4Cl.$$

The ammonium thiocyanate was added from a burette until there was a sharp fall in the resistance of the solution analyzed, accompanied by the cessation of ammonium chloride precipitation. As excess ammonium thiocyanate hampers subsequent operations, it is recommended that the volume of ammonium thiocyanate required for substitution of the chlorine atoms is first determined in a blank experiment. After the mixture of methylchlorosilanes had been titrated with ammonium thiocyanate, the substitution products obtained were titrated with 0.1 M benzene solution of dimethylaminoantipyrine. The resistance of the solution analyzed was measured after the addition of every 0.02–0.04 ml of reagent.

The nature of the conductometric titration curves for mixtures of methylthiocyanosilanes is shown in Figs. 1 and 2. Figure 1 shows titration curves for various binary mixtures of methylthiocyanosilanes. Figure 2 shows conductometric titration curves for three-component mixtures of methylthiocyanosilanes.

Analysis of the curves shows that the thiocyano derivative from the methylchlorosilane with the smallest number of chlorine atoms was titrated first. Then the dimethyldithiocyanosilane was titrated and finally methyltrithiocyanosilane, i.e., the derivative from methyltrichlorosilane, whose molecule contains the greatest number of chlorine atoms among the possible methylchlorosilanes.

The smallest amounts of methylchlorosilanes which could be determined in a mixture by the method proposed were found experimentally: not less than 0.0055 g of $(CH_3)_3SiCl$, not less than 0.0025 g of $(CH_3)_2SiCl_2$, and not less than 0.0023 g of CH_3SiCl_3 in 12 ml of mixed solvent. In the case of very high concentrations of methylchlorosilanes, the analysis solution should be diluted.

The results of quantitative analysis of binary mixtures of methylchlorosilanes are presented in Table 1.

The data in Table 1 show that two-component mixtures of methylchlorosilanes may be analyzed by conductometric titration with sufficient accuracy. The relative error of the determinations was 2%.

TABLE 1

Results of Quantitative Analysis of Binary Mixtures of Methylchlorosilanes by Conductometric Titration

Composition of mixture analyzed		Taken, g	Found, g	Error, %
A	1) $(CH_3)_3SiCl$	0,00423	0,00423	0
	$(CH_3)_2SiCl_2$	0,00320	0,00314	−2,0
	2) $(CH_3)_3SiCl$	0,00538	0,00541	+0,6
	$(CH_3)_2SiCl_2$	0,00412	0,00407	−1,3
B	1) $(CH_3)_2SiCl_2$	0,00320	0,00315	−1,7
	CH_3SiCl_3	0,00228	0,00231	+0,9
	2) $(CH_3)_2SiCl_2$	0,00412	0,00420	+2,0
	CH_3SiCl_3	0,00342	0,00346	+1,2
C	1) $(CH_3)_3SiCl$	0,00423	0,00428	+1,2
	CH_3SiCl_3	0,00228	0,00232	+1,8
	2) $(CH_3)_3SiCl$	0,00538	0,00538	0
	CH_3SiCl_3	0,00342	0,00346	+1,2

TABLE 2

Results of Quantitative Analysis of Three-Component Mixtures of Methylchlorosilanes by Conductometric Titration

Composition of mixture analyzed	Taken, g	Found, g	Error, %	Composition of mixture analyzed	Taken, g	Found, g	Error, %
1) $(CH_3)_3SiCl$	0,00423	0,00423	0	2) $(CH_3)_3SiCl$	0,00211	0,00212	+0,6
$(CH_3)_2SiCl_2$	0,00320	0,00316	−1,4	$(CH_3)_2SiCl_2$	0,00320	0,00324	+1,3
CH_3SiCl_3	0,00228	0,00231	+2,0	CH_3SiCl_3	0,00228	0,00224	−1,9

The results of quantitative analysis of three-component mixtures of methylchlorosilanes are presented in Table 2.

The data in Table 2 show that three-component systems may be analyzed quantitatively for each component of the mixture with sufficient accuracy if the concentrations of the methylchlorosilanes are not below the limits. The relative error of the determination of the individual methylchlorosilanes in the three-component mixture by the method proposed was ± 2%.

Thus, the method proposed for the quantitative determination of alkylchlorosilanes is rapid and accurate and may be used successfully for the analysis of individual alkylthiocyanosilanes and multicomponent mixtures of them, for which no differential determination methods have been described in the literature.

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SOLUBILITY ISOTHERMS OF SODIUM BOROHYDRIDE AND SODIUM HYDROXIDE IN WATER AT 0°C

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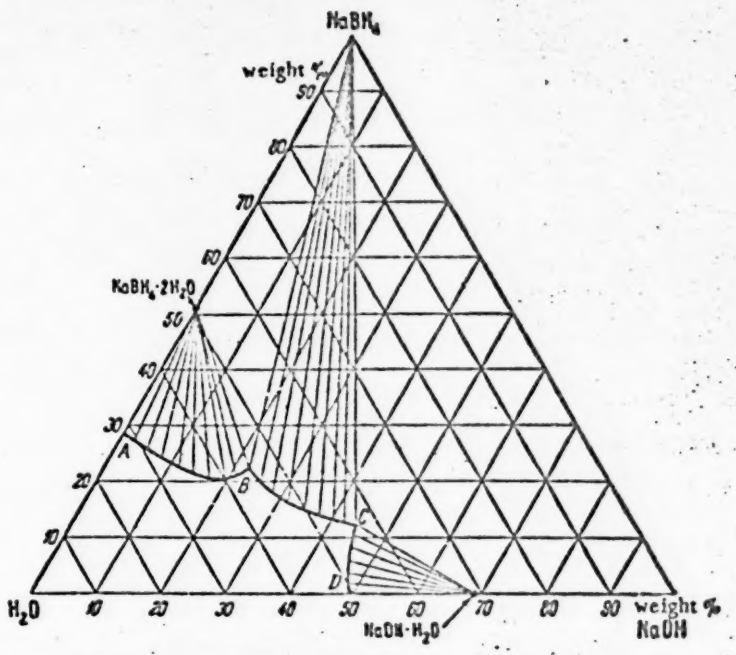
Despite the fact that it was first prepared only in 1946, sodium borohydride, $NaBH_4$, has already found wide application in recent years as a selective reducing agent, an intermediate product in the production of fuels of high calorific value, a source of diborane, and a compact hydrogen carrier [1]. Sodium borohydride dissolves readily in water with only insignificant hydrolysis. The hydrolysis of aqueous solutions of sodium borohydride may be reduced to an insignificant amount by the addition of alkali, even at temperatures above room temperature [2]. The solubility of $NaBH_4$ in 0.1 N aqueous NaOH solution in relation to temperature (0 to −50°) was studied by Jensen [3]. According to his data, the dihydrate $NaBH_4 \cdot 2H_2O$ is in equilibrium with a saturated solution of sodium borohydride at temperatures below 36.4° and anhydrous $NaBH_4$, above this temperature. The temperature of 36.4° at a pressure of 1 atm corresponds to the equilibrium of the saturated aqueous solution with the two solid phases $NaBH_4 \cdot 2H_2O$ and $NaBH_4$.

We studied for the first time the full solubility isotherms of $NaBH_4-NaOH-H_2O$ at 0°, which is of considerable interest for establishing the conditions for stabilization of aqueous solutions of sodium borohydride and for studying the conditions for isolating its crystal hydrates.

In the work we used sodium borohydride containing 99.8% of $NaBH_4$, obtained by two liquid ammonia extractions of the technical product containing 85% of $NaBH_4$, sodium hydroxide in the form of a 50% aqueous solution of chemically pure NaOH [4], and fresh distilled water. The investigation was carried out by determination of the cosolubility of $NaBH_4$ and NaOH in water under isothermal conditions with the simultaneous chemical analysis of the solid phase by Schreinemaker's method [6] and a microscopic examination of it. Glass vessels with a stirrer with an oil seal and a side arm for the removal of samples were placed in a thermostat containing a mixture of distilled water and ice to maintain the temperature at 0° with an accuracy of ± 0.1°. According to chemical analysis data, the time to establish equilibrium was 2-3 hr. The solid and liquid phases were separated by filtration through a porous filter under isothermal conditions.

The liquid phase and solid residue were analyzed chemically by titration with 0.1 N HCl to Methyl Red for determining the total alkalinity and by subsequent titration with 0.1 N NaOH in the presence of mannitol to phenolphthalein [5] for determining the boric acid formed as a result of hydrolysis of the sodium borohydride. The $NaBH_4$ content was calculated from the boron analysis data and the NaOH content was found by difference.

The solubility diagram of the $NaBH_4-NaOH-H_2O$ ternary system at 0° (Fig. 1) shows that the dihydrate $NaBH_4 \cdot 2H_2O$ crystallizes from a saturated aqueous solution of sodium borohydride A (28.9% of $NaBH_4$) as the NaOH content is increased up to a composition corresponding to point B (22.3% of $NaBH_4$ and 22.5% of NaOH), when



Isotherm for the solubility of $NaBH_4$ and NaOH in water at 0°.

anhydrous sodium borohydride crystallizes, and beginning with a composition corresponding to point C (12.3% of $NaBH_4$ and 44.4% of NaOH), sodium hydroxide monohydrate, $NaOH \cdot H_2O$, crystallizes. Apart from $NaBH_4 \cdot 2H_2O$, $NaBH_4$, and $NaOH \cdot H_2O$, no solid phases were found in equilibrium with the saturated aqueous solution.

Attention is attracted by the part of the $NaBH_4 \cdot 2H_2O$ crystallization curve adjacent to the dehydration point B. With the addition of sodium hydroxide to a saturated solution of $NaBH_4$, from the Law of Mass Action one would expect a continuous decrease in the solubility of the dihydrate. However, the latter is observed only at the beginning of the curve and then the solubility of $NaBH_4 \cdot 2H_2O$ increases appreciably with an increase in the NaOH concentration in the solution, which may be explained by the formation by the components of a complex compound that is only stable in solution.

The isotherm obtained for the solubility of sodium borohydride and sodium hydroxide in water at 0°, which is the first such diagram for a water–salt system with a borohydride anion, in addition to showing the compositions of the saturated solutions and the conditions for isolating crystal hydrate forms of sodium borohydride and sodium hydroxide, showed the crystallization of anhydrous sodium borohydride (at definite NaOH contents). The quite wide concentration region corresponding to the crystallization of anhydrous $NaBH_4$ indicated the possibility of refining technical sodium borohydride by recrystallization from aqueous solutions of sodium hydroxide.

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MECHANISM OF THE REACTION OF PHENYLIODOSO COMPOUNDS WITH SOME β-DIKETONES

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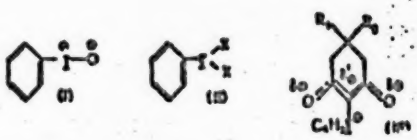
Iodosobenzene (I) and its derivatives (acetate, fluoride, and benzoate) (II, X = CH_3COO, C_6H_5OO, F) are known in organic chemistry as very strong oxidants [1-3] and as starting materials for the preparation of aryliodonium salts [4-7]. Phenyliodoso acetate (II, X = CH_3COO) is used most frequently. The reaction of phenyliodoso acetate are divided into two groups. Firstly, in reactions with alcohols, α-glycols, and amines, its oxidizing properties appear and the corresponding ketones, azo compounds, and other products are formed [1-3]. In such reactions, phenyliodoso acetate corresponds completely to lead tetraacetate and to explain the course of this reaction, Pausacker and his co-workers put forward a radical mechanism [8, 9]. The first stage of the reaction is the elimination of a molecule of acetic acid and the second is the decomposition of the intermediate product according to the following scheme:

$$R-H+\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>\!I-C_6H_5 \xrightarrow{-CH_3COOH} R-\underset{\displaystyle OOCCH_3}{\overset{\displaystyle |}{I}}-C_6H_5 \rightarrow R\cdot + CH_3COO\cdot + C_6H_5I$$

Secondly, in the presence of strong acids, phenyliodoso acetate is capable of reacting with aromatic hydrocarbons to form iodonium salts.

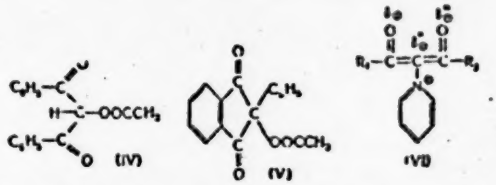
Actually, both types of reaction are based on a common scheme, which consists of the following: a) elimination of a labile proton and the formation of the corresponding derivative of dicovalent iodine, b) decomposition or stabilization of the intermediate product, which depends on the nature of the new iodine–element (C, N, or O) bond and the anion present. The reactions of phenyliodose acetate with some β-diketones investigated are in complete agreement with the mechanism presented above.

We previously reported that dimedone reacts with iodosobenzene and phenyliodoso fluoride (II, X = F) to form an internal iodonium salt of the enolate-betaine type (III, $R_1 = R_2 = CH_3$) [10].



5-Phenyl-1,3-cyclohexanedione reacts in the same way to form the corresponding iodonium derivative (III, R_1 = H; $R_2 = C_6H_5$) [11]. When this reaction was extended to other β-diketones, it was found that the iodonium

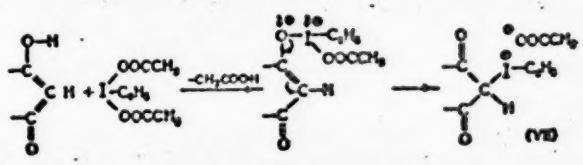
compounds could not be isolated. Acetylacetone, dibenzoylmethane, 1,3-indandione, and 2-phenyl-1,3-indandione were investigated and also acetoacetic ester and malonic ester as examples of β-keto esters. Depending on the lability of the protons of the compounds investigated, the reaction with phenyliodoso acetate proceeded with a greater or smaller heat effect and iodobenzene was formed in all cases. In the case of dibenzoylmethane and phenylindandione, the second reaction product was found to be a 2-acetoxy derivative (IV and V).



(IV) (V) (VI)

2-Acetoxydibenzoylmethane has been reported in the literature [12] and the structure of our product was further confirmed by infrared spectra. 2-Acetoxyphenylindandione was obtained by synthesis from 2-bromophenylindandione and potassium acetate and its structure was confirmed by the infrared spectrum. Indandione formed products which could not be identified. No special experiments on the acetoxylation of acetylacetone and acetoacetic ester were carried out, and the reaction of acetoacetic ester, acetylacetone, and also dibenzoylmethane with phenyliodoso acetate was carried out in the presence of pyridine. It was found that enolate-betaines of pyridinium β-dicarbonyl compounds (VI) could be isolated from the reaction products.

Such compounds could be formed as the products of heterolytic decomposition of the corresponding iodonium compounds. Consequently, it can be assumed with high probability that in the first phase of the reaction of phenyliodoso acetate with β-dicarbonyl compounds, a C-iodonium derivative is formed. It may be assumed that those β-dicarbonyl compounds which are capable of existing in an enol form react in this form with subsequent electrophilic attack of the carbon atom of the active methylene group. It is assumed that the attacking agent is the cation $C_6H_5-\overset{+}{I}-OOCCH_3$, which requires a labile proton for its formation. If salts of β-diketones are used or the reaction is carried out in the presence of proton acceptors (triethylamine or pyridine), the reaction rate is decreased considerably.



(VII)

As a result of the reaction, an iodonium salt (VII) is formed and this may be stabilized in the form of an internal salt or decompose. A typical heterolytic decomposition occurs in the presence of pyridine. The formation of acetoxy derivatives may occur both heterolytically and homolytically.

Consequently, the reaction of phenyliodoso acetate with β-dicarbonyl compounds is a new confirmation of the double reactivity of the latter and again shows the great difference between the properties of β-diketones of the 1,3-cyclohexanedione series and of the other groups investigated. The former formed only internal iodonium salts even in the presence of pyridine, while acyclic β-diketones and indandiones formed decomposition products. This difference may be explained by particular structural factors of 1,3-cyclohexanediones, for which extremely rapid secondary enolization is possible. This has been found repeatedly in the titration of the latter with bromine (100% of enol is obtained) [13]. The great similarity of the properties of 1,3-cyclohexanediones and phenols [14] may also be pointed out.

The pyridinium enolate-betaines (VI) obtained were yellow crystalline substances. The dibenzoylmethane derivative (VI, $R_1 = R_2 = C_6H_5$) has been reported in the literature [15]. The derivatives of acetylacetone (VI, $R_1 = R_2 = CH_3$) and acetoacetic ester (VI, $R_1 = CH_3$; $R_2 = OC_2H_5$) rapidly picked up moisture in air, and this caused a strong fall in the melting point. The melting points of these compounds were unsuitable for accurate characterization.

The enolate-betaines were characterized by the ultraviolet and infrared absorption spectra. The ultraviolet spectra were plotted in neutral and acid media and showed an interesting picture in comparison with the absorption

Characteristics of Substances Obtained

Substance	Color, melting point in °C, and yield in %	Found, %	Calculated %	Ultraviolet absorption maxima in CH_3OH, mμ	Infrared absorption maxima: solid, cm^{-1}	Infrared absorption maxima: $CHCl_3$ solution, cm^{-1}
2-Acetoxydibenzoylmethane	Colorless, 93–94° 94° [12] 80%	C 72,63 H 4,85	$C_{17}H_{14}O_4$ C 72,32 H 4,96		1582 (56) 1598 (70) 1691 (95) 1753 (92)	
2-Acetoxy-2-phenyl-1-1, 3-indandione	Colorless 164–165° 47%	C 72,08 H 4,29	$C_{17}H_{12}O_4$ C 71,33 H 4,20		1592 (50) 1724 (90) 1741 (89)	
Enolate-betaine of pyridinium-dibenzoylmethane	Dark yellow 212–214° 220° [15] 67%	N 4,62	$C_{20}H_{15}O_2N$ N 4,65	222 (14400) * 312 (9240)	1465–1480 (100) 1545 (80) 1581 (53) 1628 (52)	1497 (100) 1553 (44) 1626 (20)
Enolate-betaine of pyridinium-acetylacetone	Dark-yellow 172–174° 17%	N 8,03	$C_{10}H_{11}O_2N$ N 7,91	274 (19300) 312 (760) In the acid medium 256 (12600)	1544 (100) 1583 (84) 1627 (69)	1512 (89) 1582 (28) 1623 (21)
Enolate-betaine of pyridinium-acetoacetic ester	Dark-yellow 114–119° 24%	N 6,33	$C_{11}H_{13}O_3N$ N 6,76	257 (18500) 376 (850) In the acid medium 231 (8700)	1511 (80) 1627 (57) 1670 (84) 1704 (66)	1533 (65) 1624 (41) 1654 (43) 1718 (43)

* In the literature [18]: ~250 (10500) and ~320 (10500) without indication of solvent.

The value of ε is given in brackets for the ultraviolet spectra and the percent absorption is given in brackets for the infrared spectra.

of the β-dicarbonyl compounds themselves. There was a considerable hypsochromic displacement of the K-band of the enolate anion system (approximately 20 mμ), which is explained by the change in the electron structure of the enolate anion in the given enolate-betaines [11]. In an acid medium the enolate-betaines showed a strong displacement of the absorption maximum, which was connected with the formation of the un-ionized form. It is interesting that the absorption maximum of the un-ionized form of the enolate-betaine is 10 mμ below that of the enol form of the β-dicarbonyl compounds themselves and coincides with that of trans-enol ethers [16]. Consequently, the absorption of enols of acetoacetic esters and acetylacetone indicates the cis form, while the absorption of the un-ionized forms of the pyridinium enolate-betaines indicates the trans configuration of the latter. An exception is the dibenozylmethylpyridinium enolate-betaine, whose absorption spectrum in an acid medium showed only one absorption maximum around 250 mμ. This indicates decomposition of the substance, as all dibenzoylmethane derivatives are characterized by two absorption maxima [17].

The infrared absorption spectra of the enolate-betaines investigated were complex in the double-bond region and are difficult to interpret as yet. Nonetheless, it is interesting to note the typical behavior of the absorption of the carbonyl groups of the systems investigated. The pyridinium enolate-betaines of acetylacetone and dibenzoylmethane did not show absorption in the normal region for carbonyl groups. On the other hand, the derivative of acetoacetic ester showed absorption at 1718 and 1654 cm^{-1}, which indicates considerable concentration of charge on the carbon atom of the active methylene group. Consequently, the absorption spectra of the enolate-betaines investigated confirm that the localization of charge in enolate anion systems depends to a large extent on structural factors.

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** See C. B. translation.

SYNTHESIS AND SOME CATALYTIC CONVERSIONS OF PRIMARY AMINES OF THE FURAN SERIES

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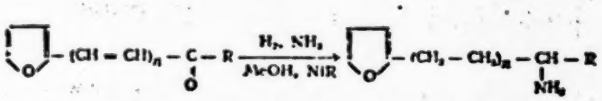
Primary amines of the furan series with the amino group in the side chain are usually prepared by catalytic hydrogenation or reduction of oximes of appropriate furan aldehydes or ketones.

Another route to the synthesis of amines consists of reductive amination of saturated and unsaturated aldehydes and ketones in the presence of ammonia. There has been little study of the application of this method to carbonyl compounds of the furan series. The preparation of furfurylamine from furfural by this method [1] and also the preparation of some furan amines from α,β-unsaturated furan ketones [2] have been reported.

By a detailed study of this method, we established that hydrogenation under pressure in an ammonia–alcohol solution in the presence of Raney nickel could be used for preparing corresponding primary furan amines not only from α,β-monounsaturated furan ketones (up to 86% of theoretical yield), but also from diene ketones (up to 84% of theoretical yield). On the example of acetylfuran, it was also shown that saturated furan ketones with the carbonyl group in position 1 relative to the furan ring are smoothly converted into primary furan amines. The furan ring was not hydrogenated under these conditions.

Thus, it was shown that this is a general reaction for converting various saturated and unsaturated furan ketones in high yields into primary amines with amino groups in positions 1, 3, and 5 of the side chain.



$n = 0, 1, 2$; R = H, CH_3, $CH_3-CH(CH_2)_n$, C_6H_5 etc.

The most important properties and analyses of the furan amines obtained in this way are given in Table 1. The table also give some physical constants of the N-acetyl derivatives of these amines, which were readily formed in up to 94% yield by the action of acetic anhydride on the amines. The hydrogenation of primary furan amines which were not substituted at the nitrogen over Raney nickel was complex. However, the N-acetyl derivatives of the amines were readily hydrogenated in dioxane solution under relatively mild conditions (Raney Ni, 80-120°, H_2 pressure up to 100 atm) to give the corresponding derivatives of tetrahydrofuran amines. The acetyl derivatives of tetrahydrofuran amines were hydrolyzed by heating with an alcohol solution of sodium hydroxide up to 170° in an autoclave.

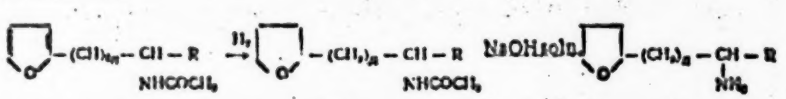


TABLE 1

Physical Constants and Analyses of Furan Amines

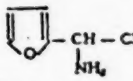
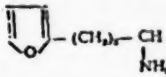
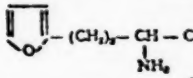
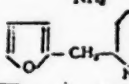
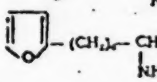
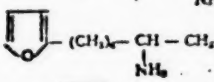
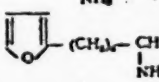
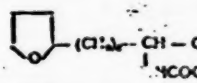
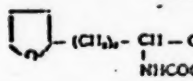
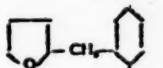
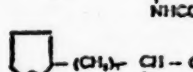
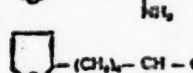
Compound	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	N, % found	N, % calc.	N-Acetyl derivatives: b.p., °C/mm	N-Acetyl derivatives: m.p., °C
	76—77/60	1.4770	0.9986	31.50	31.83	12.27 12.43	12.60	158—157/10	48—49
	85/16	1.4763	0.9629	40.77	41.07	10.23 9.90	10.08	163—168/18	54—56
	110—111/10	1.4710	0.9250	54.47	54.92	7.29 7.44	7.72	178—179/10	42—44
	119—120/10	1.5080	1.0207	52.35	52.72	7.91 7.68	7.81	172—174/3	89.5—92
	96—100/10	1.4742	0.9100	50.06	50.31	8.39 8.16	8.37	—	73—74
	132—133/10	1.4710	0.9292	63.43	64.16	6.62 7.04	6.68	197—198/10	17—18
	137/3	1.5370	1.0265	69.76	69.80	6.00 5.61	6.11	205—206/2.5	80—82

TABLE 2

Physical Constants and Analyses of Tetrahydrofuran Amines and Their N-Acetyl Derivatives

Compound	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
	135 - 141/2	1.4741	1.066	51.62	51.44	65.11 65.02	64.86	10.49 10.45	10.27	7.55	7.57
	165 - 167/4 m.p. 90 - 92	1.4725	—	—	—	67.75 67.88	67.57	10.97 10.60	10.87	6.62	6.56
	171 - 172/3.5	—	—	—	—	69.02 69.19	69.24	10.41 10.29	10.25	5.97 6.06	6.21
	93 - 96/16	1.4570	0.9253	42.15	42.08	66.95 66.93	67.13	11.43 11.46	11.58	9.87 9.40	9.79
	92 - 94/3	1.4565	0.9131	51.22	51.68	69.91 70.23	70.48	12.27 12.43	12.36	7.82 7.84	8.18

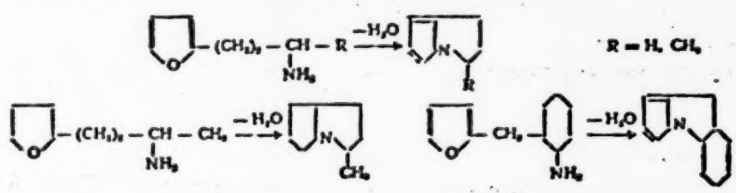
Some properties and the analyses of the tetrahydrofuran amines and their N-acetyl derivatives are presented in Table 2.

All the amines of the furan series and their N-acetyl derivatives, regardless of the position of the amino or amido group relative to the furan ring, showed intense absorption in the ultraviolet at 215-217 mμ ($\log \epsilon_{max} \sim 3.95$) and less intense absorption at 270-275 mμ ($\log \epsilon_{max} \sim 1.25$). Amines of the tetrahydrofuran series and their N-acetyl derivatives showed no selective absorption in the ultraviolet region. Infrared absorption spectra were plotted for the furan and tetrahydrofuran amines; absorption frequencies in the range 800-1500 cm^{-1} confirmed the presence of furan and tetrahydrofuran rings, respectively, while absorption frequencies in the range 3250-3450 cm^{-1} confirmed the presence of amino groups.

The furan and tetrahydrofuran amines were then used for the synthesis of pyrrolizidine and dihydrodipyrrole derivatives. These nitrogen heterocycles are present in many alkaloids.

Such substances are normally synthesized by a multistage route. Nonetheless, it is not difficult to see that the relative positions of the amino group and the oxygen atom of the ring in furan and tetrahydrofuran amines with an amino group in position 3, and beyond, in the side chain are such that they favor an intramolecular cyclization with the formation of a bicyclic system, with the nitrogen atom common to the two rings. A cyclization of this type was attempted with 1-(α-furyl)-3-aminopropane [3] over aluminum oxide at 400° but the product obtained was not characterized and the yields were not given.

We carried out experiments on the intramolecular cyclization of 1-(α-furyl)-3-aminopropane, 1-(α-furyl)-3-aminobutane, 2-furylaminocyclohexane, and 1-(α-tetrahydrofuryl)-3-aminobutane. The catalysts used were pure aluminum oxide and aluminum oxide activated with thorium dioxide, the instructions for the preparation and use of which were kindly given to us by Yu. K. Yur'ev. It was established that furan and tetrahydrofuran amines are cyclized over these catalysts to pyrrolizidine or dihydrodipyrrole derivatives according to the scheme:



The yields of dihydrodipyrroles reached 32%, while those of pyrrolizidine derivatives reached 50% of theoretical. Table 3 gives data on some physical properties and the analyses of the substances we obtained by this method. Investigations in this field are being continued.

EXPERIMENTAL

The experimental conditions are illustrated by the following examples:

Synthesis of 1-(α-furyl)-3-aminobutane. Into a 250-ml rotating autoclave were placed 40 g of freshly distilled furfurylideneacetone, 90 ml of methyl alcohol saturated with ammonia at 0°, and 5 g of Raney nickel. The reaction was carried out at 80-100° and a hydrogen pressure of 100-120 atm until the absorption of hydrogen ceased (3-4 hr). The hydrogenation product was freed from catalyst by filtration and the methyl alcohol evaporated in a nitrogen atmosphere. The residue was diluted with ether and dried with fused potassium hydroxide. The ether was removed and the residue vacuum distilled in a nitrogen atmosphere. The yield was 35-36 g (85-86% of theoretical).

The acetyl derivative was obtained by the action of 45 g of acetic anhydride on 28 g of the amine. The reaction product was neutralized with a saturated solution of sodium carbonate. The oil liberated was washed with water, dissolved in ether, and dried with fired $MgSO_4$, the ether removed, and the residue vacuum distilled.

Synthesis of 1-(α-tetrahydrofuryl)-3-acetamidobutane. Into a 150-ml steel rotating autoclave were placed 22 g of 1-(α-furyl)-3-acetamidobutane, 46 ml of dioxane, and 2 g of Raney nickel. The initial hydrogen pressure was 110 atm and the temperature 80°. Hydrogenation was complete when the calculated amount of hydrogen for the saturation of two double bonds (5.7 liters) had been absorbed. The hydrogenation product was filtered free from catalyst and the dioxane removed by distillation. The residue was vacuum distilled. The yield was 17.7 g (80% of theoretical). 1-(α-Tetrahydrofuryl)-3-acetamidobutane (29 g) was hydrolized by heating in an autoclave at 170°

TABLE 3

Physical Constants and Analyses of Some Dihydrodipyrrole and Pyrrolizidine Compounds

Compound	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	N, % found	N, % calc.
	69—70/11	1,5212	0,9870	33,07	33,13	12,56 12,38	13,07
	63—65/10 70—71/15	1,5115	0,9665	37,59	37,75	11,05 11,15	11,56
	52—53/8	1,4635	0,889	38,74	38,68	11,71 11,76	11,19
	121—123/10	1,5365	1,1016	49,55	49,40	8,19 8,42	8,7

for 10 hours in the presence of 80 ml of 2 N NaOH in methyl alcohol. The alcohol was then removed by distillation and the amine extracted from the residue with ether and dried with fired $MgSO_4$. The residue after removal of the ether was vacuum distilled.

The amines were cyclized in a flow apparatus of the usual type.

Synthesis of 3-methylpyrrolizidine. 16 g of 1-(α-tetrahydrofuryl)-3-aminobutane was passed at a rate of 5-6 drops per minute in a stream of nitrogen, through a glass tube, 40 cm long and 1.2 cm in diameter, filled with Al_2O_3·ThO_2 (5% thorium dioxide) catalyst at 325°. The liquid catalyzate was collected in a receiver, which was carefully cooled with a stream of water. The catalyzate was saturated with solid KOH and extracted with ether. The ether extract was dried with fired $MgSO_4$. The residue after removal of the ether was vacuum distilled. The yield was 6.9 g (50% of theoretical).

The infrared absorption spectra were plotted by A. D. Peshekhonova on an N-800 spectrophotometer and the ultraviolet absorption spectra on an SF-4 spectrophotometer.

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SYNTHESIS OF 1-NITROPROPYLENE AND EXAMINATION OF ITS POLYMERIZATION CAPACITY

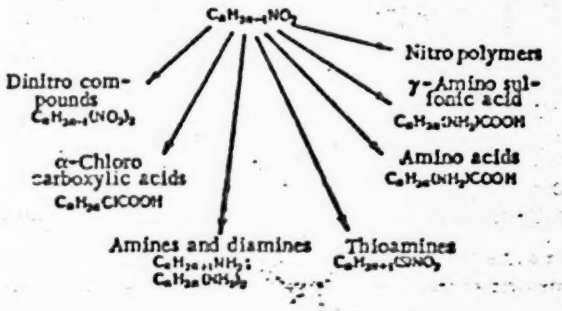
Academician A. V. Topchiev, V. P. Alaniya, and Z. A. Makarova

Translated from Doklady Akademii Nauk SSSR Vol. 131, No. 6, pp. 1359-1361, April, 1960

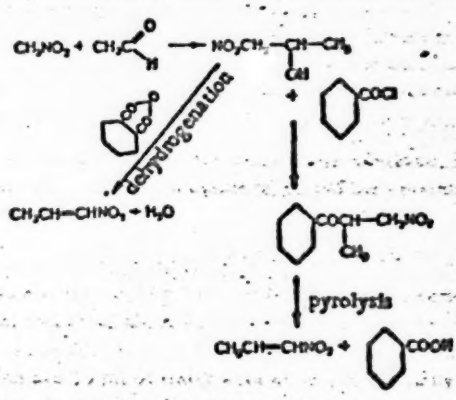
Original article submitted October 8, 1959

Nitro olefins are of interest from the point of view of their possible use for the synthesis of various products.

The main conversion of nitro olefins are as follows:



The purpose of the present work was the preparation of 1-nitropropylene from nitromethane and the examination of its polymerization capacity. 1-Nitropropylene was synthesized according to the schemes:



1-Nitropropanol was synthesized by condensation of nitromethane with acetaldehyde in 39-50% yield. The nitropropanol yield depended on the rate at which the acetaldehyde was added to the reaction mixture. 1-Nitropropylene was prepared by two methods [2, 3]: 1) by pyrolysis of 1-nitropropyl benzoate, which was obtained in

TABLE 1

Comparative Evaluation of Methods of Preparing 1-Nitropropylene

Preparation methods	Nitropropylene yield		Constants of 1-nitropropylene							
			experimental				literature			
	g	%	mol. wt	b.p., °C	d^{20}_4	$n^{20}D$	mol. wt	b.p., °C	d^{20}_4	$n^{20}D$
Pyrolysis of 1-nitropropyl benzoate	18	27.7	88	156	1.0655	1.4528				
Dehydration of 1-nitropropanol in the presence of phthalic anhydride	58.5	67	89	156	1.0654	1.4526	87	156	1.0661	1.4527

TABLE 2

Starting material	Amount of catalyst		Reaction temperature, °C	Reaction time, hr	Polymer yield, %
	g	%			
1-Nitropropylene	0.62	6	− 18	3	88
1-Nitropropylene	0.62	6	+ 20	3	33

80% yield from 1-nitropropanol and benzoyl chloride; 2) by dehydration of 1-nitropropanol in the presence of phthalic anhydride (Table 1).

The yield of 1-nitropropylene prepared from 1-nitropropyl benzoate was 28%, while the yield from dehydration of 1-nitropropanol in the presence of phthalic anhydride was 67% of theoretical. The constants of the products obtained differed little from literature data.

The possibility of polymerizing 1-nitropropylene in the presence of BF_3, a saturated solution of sodium bicarbonate, and sodium methylate was investigated. When BF_3 was used as the catalyst for polymerization of 1-nitropropylene, it was practically impossible to obtain polymers. With sodium bicarbonate solution, a polymer was obtained as a light-yellow powder, which melted with decomposition at +115°.

The investigations of the polymerization of 1-nitropropylene in the presence of sodium methylate showed that it was possible to obtain a high degree of polymerization of 1-nitropropylene in the presence of this catalyst. As the investigation showed, in this case the temperature was the main factor influencing the polymerization of 1-nitropropylene in the presence of sodium methylate. The degree of polymerization and the polymer yield increased with a fall in temperature, as is shown by Table 2.

The polymer obtained was a solid, readily combustible substance, which was insoluble in mineral and organic acids, alkalis, nitro compounds, amines, hydrocarbons, chloro derivatives, and alcohols, and partially soluble in dimethylformamide.

EXPERIMENTAL

1-Nitropropanol. Acetaldehyde (88 g, 2 mole) was added with constant stirring to a mixture of 122 g (2 mole) of nitromethane, 100 ml of 95% ethyl alcohol, and 4 ml of 10 N sodium hydroxide solution at such a rate that the temperature did not exceed 30-35°. After 2/3 of the aldehyde had been added to the reaction mixture, a further 4 ml of 10 N alkali solution and 15 ml of water were added, followed by the rest of the aldehyde. The solution was left at room temperature for 4 days. The mixture was then neutralized with hydrochloric acid and the ethyl alcohol removed by distillation. The remaining product was vacuum distilled. 1-Nitropropanol was obtained as a pale yellow, oily liquid in 39-44% yield; it had b.p. 84-86° at 5-6 mm, mol. weight 107, d^{20}_4 1.1301; $n^{20}D$ 1.4384. Literature data: b.p. 84° at 5 mm, mol. weight 105, d^{20}_4 1.1298; $n^{20}D$ 1.4378.

1-Nitropropylene (from 1-nitropropyl benzoate). A mixture of 189 g (1.8 mole) of 1-nitropropanol, 222.6 g (1.8 mole) of benzoyl chloride, and 450 ml of benzene was boiled for 12-14 hr with continuous stirring.

After the benzene had been removed by distillation at 100 mm, to the reaction mixture was added 100 ml of 95% ethyl alcohol, and the ethyl benzoate formed was removed by distillation at 100° and 20 mm.

The reddish-brown residue was dissolved in 50 ml of ether, washed and dried, and the ether removed; the 1-nitropropyl benzoate obtained was heated to 150-160° in a Claisen flask on an oil bath. The nitropropylene formed distilled under these conditions and it was purified by vacuum distillation. It had b.p. 62-64° at 45 mm, mol. weight 89, d^{20}_4 1.0655; $n^{20}D$ 1.4526. Literature data: b.p. 64° at 45 mm, mol. weight 87, d^{20}_4 1.0661; $n^{20}D$ 1.4527.

1-Nitropropylene (dehydration of 1-nitropropanol in the presence of phthalic anhydride). A mixture of 105 g (1 mole) of nitropropanol and 150 g (1 mole) of phthalic anhydride in a Claisen flask connected to a Liebig condenser was heated to 140-150° under vacuum until the mixture became homogeneous. The temperature was then raised to 175-180°. Heating was continued until distillation ceased. The distillation obtained was separated from the water and dried. The yield was 66.5% and the product had b.p. 54° at 28 mm, M 90, d^{20}_4 1.0654; $n^{20}D$ 1.4526.

Polymerization of 1-nitropropylene in the presence of BF_3. Into a flask was placed 22 g (0.2 mole) of 1-nitropropylene and BF_3 passed in (the BF_3 was obtained by the reaction $CaF_2 + 3H_2SO_4 + B_2O_3$ [4]). The reaction was carried out over the temperature range from 0 to +50°. The reaction time was varied from 30 min to 3 hr. There was practically no polymerization under these conditions.

Polymerization of 1-nitropropylene in the presence of a saturated solution of sodium bicarbonate. A mixture of 11 g (0.1 mole) of nitropropylene and 30 ml of saturated sodium bicarbonate solution was heated at 50° for 60 min with vigorous stirring. The reaction was considered complete when the mass formed acquired the temperature of the surrounding medium. The solid polymer was then collected by filtration and washed. The polymer obtained was dried in air. The polymer yield was 80% of theoretical.

Polymerization of nitropropylene in the presence of sodium methylate. The reaction was carried out in a round-bottomed flask with a mechanical stirrer, a thermometer, and a reflux condenser. After the polymerization, the flask contents were treated with acetone (at normal temperature). Treatment of the polymer with acetone formed a pasty mass. This mass was treated with water to coagulate the polymer. As a result, a solid polymer separated which was completely inert to water. The water was separated by decantation and the polymer dried in air. The yield was 86% of theoretical (at −18°).

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INVESTIGATION OF THE EFFECT OF THE COMPOSITION OF MIXED SOLVENTS ON THE RATE AND SELECTIVITY OF THE HYDROGENATION OF 2-ETHYLANTHRAQUINONE

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(Presented by Academician A. A. Balandin, November 23, 1959)

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We established previously that the rate of hydrogenation of 2-ethylanthraquinone depends essentially on the nature of the solvent. The composition of the solvent also affects the selectivity of the process. Only one mole of hydrogen was absorbed in N,N-dimethylformamide, while in dioxane, for example, the reaction did not cease after the absorption of a mole of hydrogen, i.e., the aromatic nucleus of anthraquinone was also hydrogenated at an appreciable rate. The choice of solvent is of exceptional importance in the industrial process for the production of hydrogen peroxide by the quinone method [1]. A number of patents have been devoted to this problem. However, the effect of medium on the rate and direction of the reaction have not been examined in them.

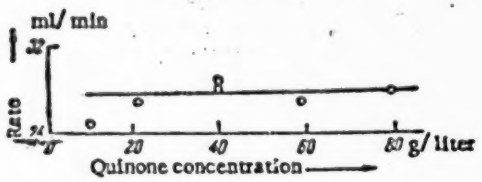

Fig. 1. Relation between the rate of hydrogenation of 2-ethylanthraquinone and its concentration in dimethylformamide.

In the present work we studied the relation of the rate and selectivity of the process to the nature of the solvents and especially the composition of the mixed solvents dioxane—N, N-dimethylformamide and dioxane—ethyl alcohol. The reaction was carried out in a hydrogenation flask over a skeletal nickel catalyst at 20°. The catalyst was prepared by leaching an Ni—Al alloy (50:50) at 25° with subsequent heating on a steam bath for 12 hr. The catalyst was dried before an experiment by washing with the appropriate solvent. The dioxane was freed from peroxides and other impurities by treatment with hydrochloric acid solution and then alkali and was distilled over metallic sodium in a stream of nitrogen [2]. The dimethylformamide was freed from amine salts by repeated treatment with solid alkali and vacuum distillation [3]. The ethyl alcohol was dried with metallic calcium. For each experiment we used 0.300 g of catalyst and 2.37 g of 2-ethylanthraquinone (m.p. 107-108°) in 30 ml of solvent. The reaction rate was measured by the rate of hydrogen absorption. In separate experiments, samples were taken during the reaction for polarographic analysis of the catalyzate for quinone content after oxidation by air. The analysis was carried out on an LP-55 automatic photopolarograph by the procedure in [4], which made it possible to determine 2-ethylanthraquinone, 2-ethyltetrahydroanthraquinone, and 2-ethyloctahydroanthraquinone when present together. The half-wave potentials of the quinones in 80% methyl alcohol were 0.75, 0.55, and 0.40 v, respectively.

Preliminary experiments showed that for the solvents studied and under the conditions chosen, the reaction rate was independent of the mixing rate at > 200 vibrations per minute. The experiments described in the present

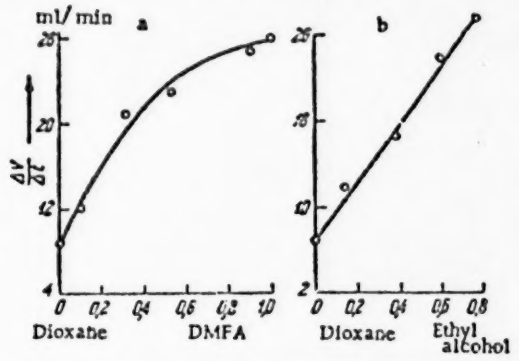

Fig. 2. Relation between the rate of hydrogenation of 2-ethylanthraquinone and the solvent composition (in moles): a) dioxane–dimethylformamide; b) dioxane-alcohol.

work were carried out with vigorous mixing (800 vibrations/min). With the given amount of catalyst, the reaction rate remained constant in all the solvents tested up to 80% conversio of the 2-ethylanthraquinone to 2-ethylanthrahydroquinone. The zero order of the reaction in dimethylformamide was also confirmed by theconstancy of the hydrogen absorption rate with a change in quinone concentration from 10 to 80 g/liter (Fig. 1). A deviation from zero order was observed only during hydrogenation in dioxane alone after the absorption of 0.3 mole of hydrogen.

Figure 2 shows the relation between the rate of absorption of the first mole of hydrogen and the composition (expressed in moles) of the binary solvents dioxane–dimethylformamide and dioxane–alcohol. Figure 2,a shows that with a change from dioxane to dimethylformamide the reaction rate increased by a factor of 3-3.5. There was a particularly large increase in the rate of the process with the addition of up to 20-30 mol. % of dimethylformamide to the dioxane. A further increase in the dimethylformamide concentration in the mixed solvent had a smaller effect on the reaction rate. In contrast to this, in the mixed solvent dioxane–alcohol there was a linear relation between the reaction rate and the content of the polar component, i.e., alcohol (Fig. 2,b). In the solvent dioxane–alcohol (72% alcohol) the reaction rate was 4.5 times greater than in dioxane alone. The second and third moles of hydrogen were not absorbed in dimethylformamide, while in the other solvents the rate of their absorption was considerably less than for the first mole.

As has been stated, the selectivity of the process also depended on the nature of the solvent. This could be assessed from the volume of hydrogen absorbed, the change in the nature of the kinetic curve, and the change in potential of the catalyst during hydrogenation. However, two important questions remained unsettled: whether one or both of the aromatic rings of the quinone were hydrogenated and at precisely what stage this occurred, i.e., from the very beginning of the reaction or only after a considerable concentration of hydroquinone (quinhydrone) in the solution had been reached. These questions are also of practical interest as tetra- and octahydroquinones are formed by hydrogenation of the nucleus and these have properties that are quite different from those of the starting quinone. The use of polarography made it possible to give an answer to these questions. As polarographic analysis data showed, apart from the hydroquinone, only 2-ethyltetrahydroanthrahydroquinone was formed under the conditions of our experiments. Right up to the absorption of 3 moles of hydrogen, the wave at 0.40 v was absent from the polarogram, i.e., 2-ethyloctahydroanthrahydroquinone was not formed.

Table 1 shows that the reaction was least selective in dioxane. Even under mild experimental conditions (at 20° and normal pressure) the formation of 2-ethyltetrahydroanthrahydroquinone began. After the absorption of 0.3 mole of hydrogen, the reaction products were found to contain 1% of tetrahydroquinone; after the absorption of 0.5 mole of hydrogen, 2%; after 0.75 mole of hydrogen, 4%; and after 0.95 mole of hydrogen, 8% of tetrahydroquinone. Thus, tetrahydroanthrahydroquinone was formed mainly after the absorption of 0.5 mole of hydrogen. The addition of 1% alcohol to the dioxane increased the specificity of the process somewhat; after the absorption of 0.5 mole of hydrogen, 1% of 2-ethyltetrahydroanthrahydroquinone was formed, and after the absorption of 0.95 mole of hydrogen, 5%. In hydrogenation in a solvent containing 90% of dioxane and 10% of alcohol or equal volumes of dioxane and alcohol, tetrahydroquinone was not detected in the reaction products even after the absorption of 0.95 mole of hydrogen.

In contrast to dioxane, the reaction in dimethylformamide was completely selective; one mole of hydrogen was absorbed and only the quinone groups were hydrogenated. It is especially interesting that the process was also selective when 1% or even 0.3% of dimethylformamide was added to dioxane. The strong effect of such a small amount of added material is apparently explained by the fact that dimethylformamide is selectively adsorbed on the catalyst and displaces the hydroquinone or quinhydrone formed from its surface. As we showed recently,

Degree of Conversion of 2-Ethylanthraquinone into 2-Ethyltetrahydroanthrahydroquinone (in percent)

Solvent composition	Hydrogen consumption in moles				
	0.3	0.5	0.95	2.0	3.0
Dioxane	1	2	8	45	98
Dioxane 99% + alcohol 1%	•	1	6	50	98
Dioxane 90% + alcohol 10%	•	•	•	48	98
Dioxane 50% + alcohol 50%	•	•	•	48	92
Dioxane 99.7% + dimethylformamide 0.3%	•	•	•	42	90
Dioxane 99% + dimethylformamide 1%	•	•	•	40	95
Dimethylformamide	•	•	•	Not absorbed	

Note. The sign • denotes < 0.2% as it was possible to determine down to 0.2% of 2-ethyltetrahydroanthrahydroquinone in 2-ethylanthraquinone polarographically under our conditions.

pyridine acts similarly but with the difference that pyridine probably displaces not only the hydroquinone formed, but also the starting 2-ethylanthraquinone, so that the reaction rate falls sharply in its presence. As has already been stated, the action of dimethylformamide, in contrast to that of pyridine, is remarkable in that not only is hydrogenation of the nucleus suppressed in its presence, but also the rate of reduction of the quinone groups increases. However, this effect changes strongly with a change in the concentration of dimethylformamide in the mixed solvent, while a very small amount of it is sufficient to make the process selective.

Thus, the composition of the mixed solvent has a substantial effect on the rate and selectivity of the process. Dioxane promotes hydrogenation of the nucleus of 2-ethylanthraquinone. Only one of the two aromatic rings is hydrogenated in dioxane at 20° and normal pressure and no octahydro derivative is detected. The tetrahydro derivative is formed from the very beginning of the process and its formation is accelerated after the absorption of 0.5 mole of hydrogen. The addition of a polar component to the dioxane leads to an increase in the rate of reduction of the quinone groups and suppression of hydrogenation of the quinone nucleus. When even a small amount of dimethylformamide (0.3%) is added to dioxane, hydrogenation of 2-ethylanthraquinone proceeds selectively. The increase in the selectivity of the process is apparently caused by the increase in rate of hydrogenation of the quinone groups and adsorptive displacement of hydroquinone molecules. The degree of selectivity in this case depends on the nature and amount of the added polar solvent.

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STRUCTURE OF 9-AMINOACRIDINE

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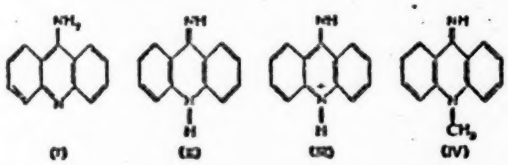
Arguments in favor of both an amino (I) [1-5] and an imino (II) [6-9] structure for 9-aminoacridine have been presented in the work of various authors.



(I) (II) (III) (IV)

Data from infrared spectra have been used in some of this work [3, 6, 7] and these spectra have been examined in more detail in the work of A. V. Karyakin and A. V. Shablya [8], who put forward a hypothesis on an intraionized imino structure for 9-aminoacridine (III). The authors based this idea on the closeness of the ν(N–H) bands in the infrared spectrum of 9-aminoacridine, 9-acridone and acridinium hydrochloride, and on the assignment of the bands at 1650 cm^{-1} and 1570 cm^{-1} in the spectrum of 9-aminoacridine to deformation oscillations of C–$\overline{N}$–H and $\geqslant\overset{+}{N}$–H groups, respectively.

However, objections have been raised to the assignments of bands in the spectra made by these authors and the conclusions drawn from them. Thus, in recent work of Mason [10] it was shown that the position of ν(N–H) bands in the spectrum of 9-aminoacridine agree well with an amino rather than an imino structure for this compound. The assignment of the band at 1570 cm^{-1} to the deformation oscillation of $\geqslant\overset{+}{N}H$ contradicts the systematic presence of this band in the spectra of most heterocyclic amines and other isomeric aminoacridines which have an amino structure and therefore do not contain an $\geqslant\overset{+}{N}H$ grouping. The assignment of the second band at 1650 cm^{-1} is not supported at all in [8] by any comparisons and is not in agreement with literature data [11].

The inaccuracy of the assignment of the band at 1650 cm^{-1} to the deformation oscillation of C–N–H is also shown by the infrared spectrum we obtained for N-methyl-9-acridonimine (IV), which definitely has an imino structure. There were no absorption bands in this region in the spectrum of this compound and the first intense absorption band was observed at 1613-1600 cm^{-1} (Fig. 1) and, as will be seen from what follows, this cannot be assigned to the deformation oscillation of C–$\overline{N}$–H, but is obviously caused by the valence oscillation of the exocyclic C = N bond.

If it is assumed that 9-aminoacridine has an amino structure, the band at 1650 cm^{-1} may be assigned to the deformation oscillation of NH_2 and the band at 1570 cm^{-1} to the oscillation of the heterocyclic nucleus of the molecule. Nonetheless, the bands examined may also be interpreted satisfactorily if an imino structure is adopted

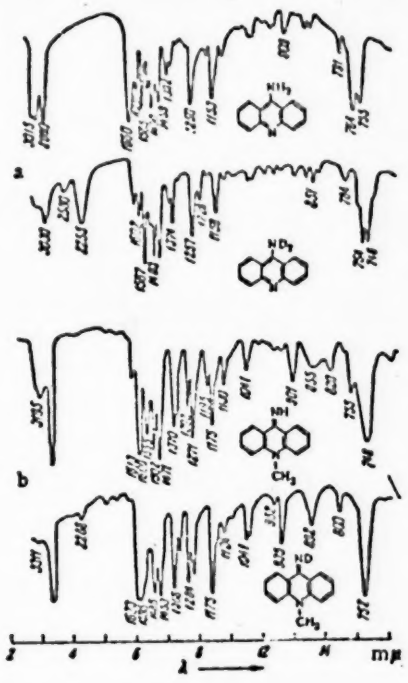


Fig. 1. Infrared spectra: a) 9-aminoacridine; b) N-methyl-9-acridonimine and their N-deutero derivatives.

(the band at 1650 cm^{-1} is assigned to the valence oscillation of the excyclic imine bond C = N and the band at 1570 cm^{-1} to the oscillation of the heterocyclic nucleus or the deformation oscillation of C = N−H). It seemed to us that it would be possible to choose the correct assignment for the bands at 1650 and 1570 cm^{-1} in the spectrum of 9-aminoacridine and, consequently, solve the problem of the structure of molecules of this compound by examining the changes in the infrared spectrum of 9-aminoacridine on deuteration of its amino group. Actually, if 9-aminoacridine is an amine, deuteration should produce a sharp displacement of the band at 1650 cm^{-1} in the infrared spectrum toward longer wavelengths as the frequency of this oscillation depends directly on the mass of the atoms participating in the oscillation. If the compound investigated an imine and the band examined is caused by valence oscillations of the exocyclic C = N bond, then deuteration could produce only a slight displacement of the corresponding band.

Data available in the literature on aliphatic amines and aniline [12, 13] show that with deuteration, the band of δNH_2 (at 1620–1630 cm^{-1}) actually disappears and a new band, evidently caused by oscillations of δND_2, appears in the region of 1190–1200 cm^{-1}. The latter band is of low intensity in the case of N-deuteroaniline. Exactly the same picture was observed when we compared the spectra of a number of heterocyclic amines with the spectra

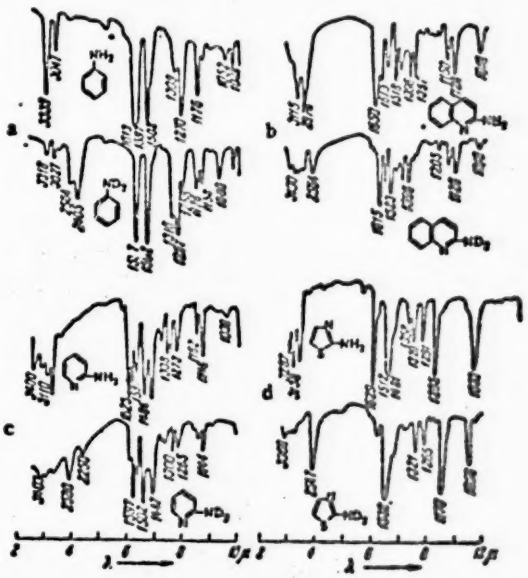


Fig. 2. Infrared spectra: a) aniline; b) 2-aminopyridine; c) 2-aminoquinoline; d) 2-aminothiazole and their N-deutero derivatives.

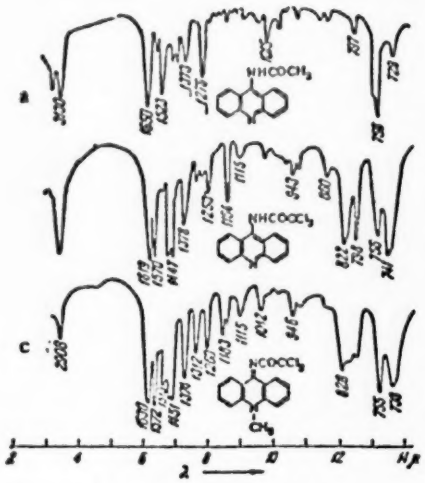


Fig. 3. Infrared spectra: a) 9-acetylaminoacridine; b) 9-trichloroacetylaminoacridine; c) N-methyl-9-trichloroacetylacridonimine.

of their N-deutero derivatives (Fig. 2): The δNH_2 band of these compounds (1620-1650 cm^{-1}) disappeared practically completely on deuteration and no new absorption bands appeared in the immediate vicinity. The bands at 1530-1600 cm^{-1}, which were evidently caused by oscillations of the heterocycles, remained practically unchanged. When 9-aminoacridine was deuterated, the absorption band at 1660 cm^{-1} also disappeared, while the band at 1565 cm^{-1} remained unchanged (bands at 1650 and 1570 cm^{-1} according to [8]).

The deuteration of N-methylacridonimine, a substance with a definite imine structure, had hardly any effect on the position of its most intense double band (1600-1613 cm^{-1}) and produced only a slight broadening (1623-1595 cm^{-1}) (Fig. 1). The band at 1555 cm^{-1} also disappeared.

From the data presented, it follows that the band at 1600-1613 cm^{-1} ($\nu C=N$), which does not change on deuteration) and the band at 1555 cm^{-1} ($\delta C=N-H$, which moves to another region on deuteration) correspond to a compound with an imino structure and both of these bands are absent from the spectrum of 9-aminoacridine. The bands at 1660 cm^{-1} (δNH_2, which is displaced to another region on deuteration) and 1565 cm^{-1} (oscillation of the heterocyclic nucleus, which is unchanged on deuteration) correspond to an amine structure and both of these bands are present in the spectrum of 9-aminoacridine. Thus, from the results obtained it follows that 9-aminoacridine is an amino compound.

Other, independent confirmation for this conclusion is provided by an examination of spectral data for 9-acetylaminoacridine. Were 9-aminoacridine an acridonimine, its monoacetyl derivative should have an imino structure all the more definitely, as the acidifying action of the acetyl group could only increase the tendency for the compound to exist in the imino form [15].

However, the infrared (Fig. 3) and ultraviolet spectra unequivocally show that 9-acetylaminoacridine has an amino structure (see also [14]) and, consequently, 9-aminoacridine has an amino structure.

Only the introduction of a considerably stronger acidifying substituent (a trichloroacetic acid residue) into the amino group of 9-aminoacridine causes the appearance of the acridonimine form in solutions and the conversion of the compound into this form in crystals (Fig. 3). From an evaluation of the content of the imino form of 9-trichloroacetylaminoacridine in solutions, it may beconsidered that with respect to the tendency to change into the imino form, 9-amonoacridine occupies an intermediate position between 2-aminoquinoline and 2-aminothiazole [15], for which, according to approximate data [16], the value $K_T \frac{\text{imine}}{\text{amine}}$ in solutions is of the order of 10^{-5}.

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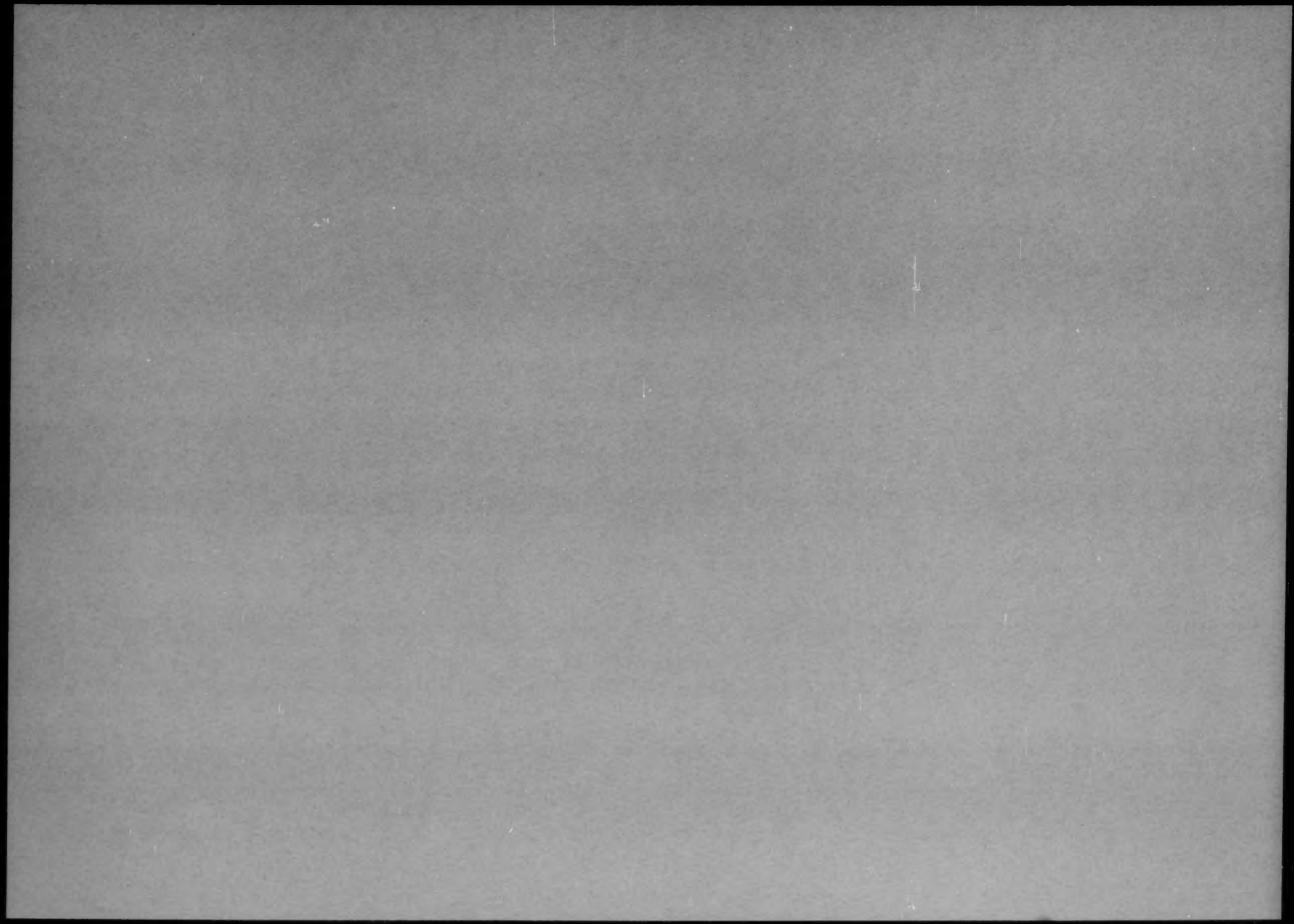
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